about

water treatment

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Content

About water treatment

Water is our most vital form of sustenance. It is important that we return the water we borrow from nature in such a condition that it does not cause pollution.

Clean water will be an important economic and political issue in the future. The availability of clean water will be crucial for mankind's development in many important respects.

"About water treatment" is a book that describes the methods and processes that are used today for treating potable water and wastewater. It also looks at the problems surrounding sludge and the ways in which it is processed.

The book describes methods of water treatment that allow water to be returned to its natural ecological cycle and permit a sustainable society. We hope that this book gives the reader a complete picture of water treatment.

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We would like to hear your ideas, comments and suggestions at: www.kemira.com

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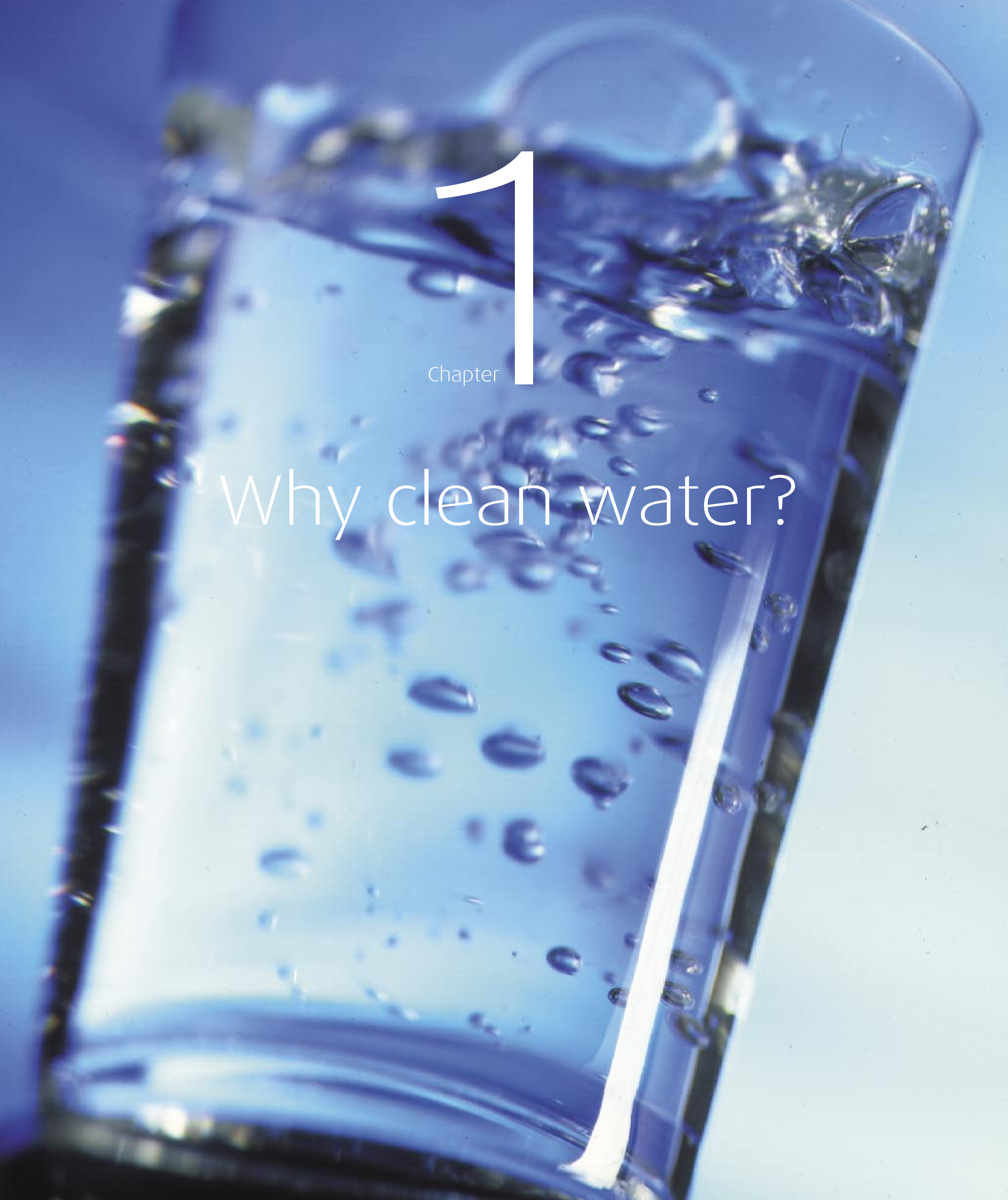


Chapter 1 Why clean water?

Why clean water?

Water is our most vital form of sustenance. Every living creature on the Earth depends for its survival on access to water. The body of an adult man contains around 60% water, while a woman's contains around 55%. The availability of water has played and will continue to play a major role in the development of society.

The water on our planet is purified and recirculated in a gigantic solar-powered eco-cycle. Evaporation transfers the water to the atmosphere and it is returned to the soil by condensation and precipitation. This distillation process regulates the temperature on the Earth. It cools the soil and the seas, and warms the atmosphere.

Of all the water on the Earth, 98% is salt water, 1,6% is ice, 0,4% is ground water and 0,004% is surface water. The availability of water to mankind is unevenly shared across the continents. The scarcity of water in large areas leads to disease and death. Population growth, urbanisation and the increasing use of water mean that the natural cycle of purification is inadequate to safeguard the availability of clean water. Nowadays it is no longer sufficient just to treat potable water; it is vitally important that we also treat wastewater in order to protect our waterways and reservoirs.

In other words the treatment of wastewater is the key to healthier potable water.

> ”Water is a friendly element to those
> who are familiar with it
> and know how to handle it.”
>
> Johann Wolfgang Goethe

Only a limited amount of the water on Earth is available to mankind – water that circulates in a never-ending eco-cycle.

Potable water treatment

Clean water and good personal hygiene should be considered essential if people are to maintain good health. Some estimates suggest that 80% of all illnesses and more than one-third of all deaths in developing countries are a result of drinking contaminated water.

Microbiologists talk about three main types of illness: waterborne, hygiene-related illness and water-related.

In order to ensure a hygienically acceptable supply of water that tastes good, both the surface water and the ground water in industrialised countries are treated in **water purification plants** before the water is distributed to the consumer.

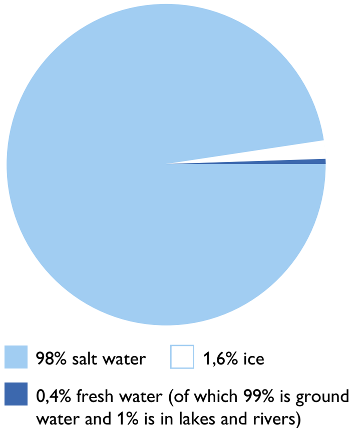
The production of potable water is an industrial process governed by strict inspection requirements. In comparison with other branches of industry it turns out that water production is by far the largest in terms of the annual tonnage produced.

Industrialised countries produce up to 150,000 litres of water per person per year (around 400 litres per person per day). The water they produce must also meet requirements to guarantee its suitability as drinking water, even though only around 3% (10 litres per person per day) is used for food and drink.

Potable water is produced from **surface water**, i.e. water from lakes and waterways, or **ground water**, which comes from the soil and rock. It is also possible to use sea-water as a source of raw water, if it is desalinated.

Ground water is often the best source of raw water, since it is filtered naturally and has a low concentration of bacteria and organic contaminants. In densely populated areas there is generally an inadequate supply of ground water, so surface water must also be used as a source of raw water.

The proportions of surface water and ground water that are used vary widely from country to country. Usually, however, the majority of potable water is produced from surface water. In the EU countries, for example, the ratio is 64% surface water to 36% ground water.



➤ **Figure 1:1** The distribution of water on Earth.

Wastewater treatment

The wastewater that we produce is collected by the sewage network and transported to the wastewater treatment plant, then returned to the natural eco-cycle by discharging into waterways. This municipal wastewater contains a large number of different contaminants and its composition varies from place to place. This depends on various factors, including the degree of urbanisation and the type of industry and public utilities in the area.

Municipal wastewater consists of a mixture of used potable water (from household sinks, bathrooms, toilets and from industry), leaking ground water plus rainwater and melt water. The composition and flow rate actually varies within a given geographical area from hour to hour, day to day and season to season.

Wastewater has traditionally been treated using mechanical and biological processes.

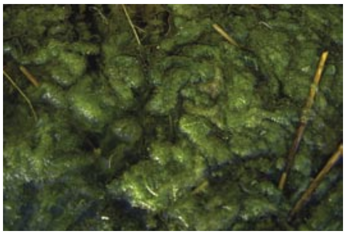
Decomposition

When organic matter from wastewater is discharged into a waterway, or recipient, the material is broken down by a variety of microorganisms, generally bacteria, which also consume the available oxygen in the water. This process is known as decomposition.

During the forties and fifties, attention was focused on trying to reduce the proportion of oxygen consuming substances, such as organic matter and, later on, ammonium, in order to gain control over the decomposition process. For many years the parameters BOD (Biochemical Oxygen Demand) and SS (suspended solids) were specified in emission requirements for wastewater treatment plants. In some cases, where maintaining the oxygen balance of the recipient was a particularly severe problem, requirements were also imposed on nitrification.

Eutrophication

Despite the growing use of biological treatment plants and treatment requirements based on BOD, SS and in some cases nitrogen, as measured by nitrification, many waterways have still suffered negative effects. In many cases this is due to the growth of algae, often referred to as the secondary organic load, which require a great deal of oxygen to break down. Algal growth is promoted by the discharge of **phosphorus** and **nitrogen** (nutrient salts), which are not removed by the conventional biological treatment process.



Bildtext

One major international problem is the **eutrophication** (over-fertilisation) of lakes and waterways, i.e. a large increase in the concentration of nutrients that causes rapid growth in the populations of some aquatic organisms.

For example, one gram of phosphorus can give rise to around 1700 grams of plant matter (algae), which is equivalent to around 140 grams of dry algae. When these algae decompose they consume oxygen, partly through the oxidation of carbon into carbon dioxide, and partly through the oxidation of nitrogen into nitrate. The oxygen required for complete oxidation is approximately 5 grams of oxygen per gram of carbon, and 3 grams of oxygen per gram of nitrogen.

The respective weight ratios of phosphorus, nitrogen and carbon in algal matter are approximately 1 : 7 : 40.

The nutrients present in untreated municipal wastewater can therefore lead to the secondary consumption of more than five times as much oxygen as is required to decompose the primary organic matter in the wastewater. It is therefore important to reduce the concentration of nutrients in the wastewater before it is discharged into the recipient.

Phosphorus reduction has been introduced in most large European treatment plants since phosphorus was first identified as the most significant factor in the growth of algae. A marked improvement has been seen in most recipient waterways as a result of the reduction in phosphorus levels.

Despite the introduction of phosphorus reduction in treatment plants, fish have died in large numbers and there have been massive algal blooms along coastlines. In seawater it turns out that nitrogen plays a major role in eutrophication. Phosphorus is however still regarded as the dominant factor in the eutrophication of lakes and waterways.

Red tide is an environmental problem that was first noticed in the latter half of the nineties, mainly in the Mexican Gulf and along some Asiatic and European coastlines. Red tide is a mat-like growth of an alga that produces a toxin which kills large numbers of fish. The name comes from the red colour that the algae impart to the sea. Nutrient salts, especially phosphorus, are now considered to be the cause of the problem, which occurs where large rivers discharge their nutrients into the sea.

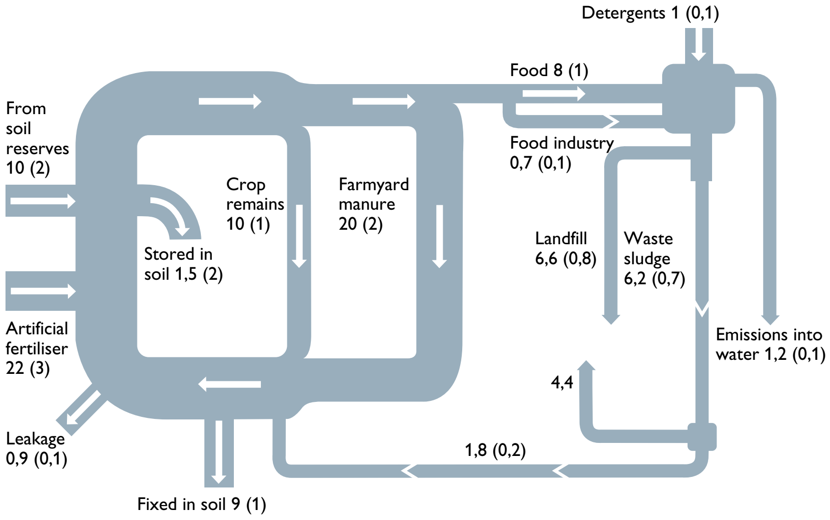
Phosphoros

Each person contributes approximately 2–3 g of phosphorus to wastewater each day. Most of it comes from faeces and urine, with around a third from detergents. The recipient also receives some phosphoros from agriculture. However, in the case of agriculture it is nitrogen that is the most significant component in run-off water from cultivated land.

Phosphorus is classified into three main fractions: **orthophosphates**, **polyphosphates** and **organically bonded phosphorus**. When we talk about the total concentration of phosphorus we mean the sum of these three fractions.

Phosphorus from detergents in wastewater occurs as polyphosphates. These are hydrolysed relatively quickly in wastewater to form orthophosphates. The majority of the phosphorus that is present in faeces and urine is already in the form of orthophosphates. 30–50% of the phosphorus is bound up in organic compounds (in colloidal or suspended substances).

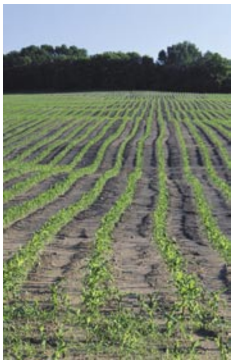
The reduction in phosphorus that a conventional biological treatment plant can achieve is nowhere near sufficient to prevent the growth of organic substances. In the mechanical treatment stage up to 30% of the incoming phosphorus, which is bound up in suspended substances, can be separated. A large proportion of this phosphorus is however returned to the treatment process after sludge stabilisation and dewatering.



➤ **Figur 1:2** The flow of phosphorus in Swedish agriculture and society. The figures give the amounts in thousands of tonnes of phosphorus per year, and in brackets in kilograms per person per year.

Source: Olle Pettersson, Swedish University of Agricultural Sciences.

The name phosphorus comes from the ancient Greek: "to give light". Phosphorus does not occur naturally as an element, but is generally bound up with oxygen as phosphate. The element is present in around 200 different minerals and is essential for both plants and animals.



Nitrogen is the sixth most common element in the universe. On the Earth there is nitrogen in the atmosphere, the Earth's crust, the hydrosphere and the biosphere. Dry air contains around 78 percent nitrogen by volume.

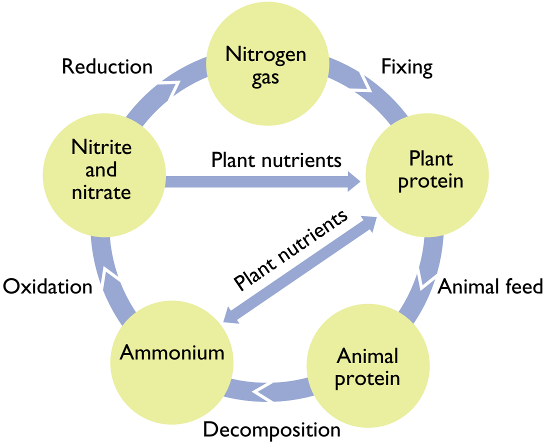
The biological treatment stage requires phosphorus in order to support the growth of microorganisms. The biomass in the biological sludge contains around 2% phosphorus. Roughly one gram of phosphorus is required to break down 100 grams of BOD. In total, a conventional biological treatment plant can remove at most 20–30% of the overall phosphorus content of the wastewater.

The phosphorus content can be reduced chemically as well as biologically. In Scandinavia, parts of central Europe and around the Great Lakes in North America, the bulk of phosphorus reduction is achieved using various forms of chemical precipitation.

Nitrogen

The nitrogen load on our waterways comes mainly from atmospheric deposition and from agriculture. Municipal waste accounts for less than 20%.

Nitrogen has a natural cycle. Ammonium salts and nitrates are both easily accessible sources of nitrogen for the production of plant cell matter by nitrogen assimilation.



➤ **Figure 1:3** The nitrogen cycle.

➤ **Table 1:1** Nitrogen in various forms.

Nitrogen in various forms	
Nitrogen gas (N_2)	Pure nitrogen. Makes up 78% of the Earth's atmosphere.
Ammonium (NH_4^+)	Decomposition product of organically bonded nitrogen. Provides an easily accessible nutrient source for both land-based and aquatic plants. May form ammonia.
Ammonia (NH_3)	Poisonous gas, soluble in water. Formed from ammonium ions in water with high pH.
Nitrate (NO_3^-)	Oxidation product. Forms salts in combination with various metals. Easily accessible nutrient source for plants.
Nitrite (NO_2^-)	Intermediate stage in the oxidation of ammonium to form nitrate.
Proteins	Large molecules that form the building blocks of all living tissue in plants, animals and people. Nitrogen is an essential component of all proteins, together with carbon, hydrogen and oxygen.

Because nitrogen compounds such as ammonium, nitrite and nitrate occur in soluble form they would accumulate in lakes and seas if the nitrogen were not removed on an ongoing basis. This happens naturally on a large scale due to the oxidation of ammonium to produce nitrite or nitrate, in a process known as nitrification. The nitrite and nitrate are then reduced to nitrogen gas, which returns to the atmosphere in a process known as denitrification.

Conversely, atmospheric nitrogen can be fixed by microorganisms. This is the origin of a large proportion of all bound nitrogen.

High concentrations of nitrate in water are a health hazard and can be very dangerous for infants, since the nitrate can convert into more toxic nitrite.

Nitrosamines, which are formed from nitrate and nitrite, are carcinogenic at high concentrations. Ammonium can also be poisonous since it forms ammonia in solutions with a high pH. Water with a high pH and high concentration of ammonium is toxic to fish.

Nitrogen can be removed from wastewater using biological and chemical-physical methods. Chemical methods are often more costly than biological methods. They are used where biological methods are ineffective, for example on difficult industrial wastewater.

Chapter 2

Potable water treatment

Chapter 2 Potable water treatment

Potable water treatment

In most cases the sources from which we obtain our water are not clean enough to allow human consumption without any prior treatment. A variety of treatment methods must be employed, depending on the levels of undesirable substances in the raw water and on the demands set for water purity.

The first priority for the water supplier is to distribute water that meets the requirements of the authorities, which are based on health-related considerations. Potable water must not contain harmful bacteria or viruses, toxic inorganic metals or organic compounds, such as pesticides. The aesthetic characteristics of the water must also be considered, and it must therefore meet certain requirements regarding colour, turbidity, odour, taste etc.

Because of the breadth of knowledge that has been amassed in water treatment technology, and the equipment and products that are available today, there are excellent opportunities to produce potable water that will satisfy the most demanding consumer and the strictest requirements, even with raw water of poor quality.

Groundwater as a source of raw water

Groundwater forms as a result of water infiltrating through the ground. Carbon dioxide is formed by the breakdown of organic matter (plant remains) that is dissolved in the water. During the passage of the water through the various strata its content,




"When you drink water,
think of its source."

Chinese proverb

Life on Earth began in the water around 3000 million years ago. Today, everything living on the planet needs water to survive.

of humic substances, colour and cloudiness decrease. The concentrations of bacteria, viruses and single-cell organisms (protozoa) also decrease.

The water dissolves minerals that contain metals such as magnesium, calcium, sodium, iron and manganese. The concentrations of sulphates, chlorides and carbonates also contribute to the characteristic composition of groundwater.

Groundwater can in some cases meet acceptable standards of quality without any special treatment. In order to protect distribution piping it may be necessary to make the water alkaline and limit the bacteria content by disinfecting it. Alkalisation and disinfection are therefore final stages in most waterworks.

In those cases where groundwater requires more extensive treatment, table 2:1 shows the most common undesirable substances, their negative effects and how they are neutralised or removed.

➤ **Table 2:1** Undesirable substances in groundwater.

Undesirable substance	Treatment method
Carbon dioxide, CO_2 (acid water) - causes corrosion in piping	• **Add chemicals to increase alkalinity** • **Increase alkalinity by filtering through alkaline material** • **Aeration**
Iron (Fe^{2+}) and manganese (Mn^{2+}) - turbidity, odour and bad taste - gives deposits/sludge in piping	• **Oxidation by aeration, addition of chlorine, potassium permanganate or ozone and filtration**
High hardness (Ca^{2+}, Mg^{2+}) - causes deposits	• **Ion exchange using cationic exchange unit** • **Precipitation with lime or other alkali**
Nitrate (NO_3^-) nitrite, (NO_2^-) - impairs oxygen uptake by blood	• **Ion exchange using anionic exchange unit** • **Biological methods**
Fluorine, (F^-) - discoloration of teeth	• **Adsorption by activated aluminium oxide** • **Precipitation with aluminium sulphate or lime** • **Filtering through anionic exchange medium**
Pesticides	• **Adsorption by activated carbon** • **Breakdown through oxidation with ozone or hydrogen peroxide** • **Biological breakdown**

Surface water as a source of raw water

Lakes are the Earth's water store. Lake water is soft and has a low salt content.
It often contains algae, humus and other organic substances that can give it colour, odour and taste, and it must therefore be treated.

Surface water is the name given to water found in streams, rivers and lakes. Lakes are important because of their ability to store water. The characteristic of water that makes it a good solvent also means that it is easily contaminated and consequently is rarely clean enough to use without prior treatment. This is partly due to nature and partly due to man. The most common contaminants are:

Humic substances, which is the breakdown products of plants, gives water a yellow to golden-brown colour and can give an undesirable odour and taste.

Mineral particles, which are natural contaminants, consist of fine particles such as clay. These make the water cloudy. This cloudiness is measured as turbidity and can be expressed in **F**ormazin **T**urbidity **U**nits (FTU) or **N**ephelometric **T**urbidity **U**nits (NTU). These units are directly comparable, i.e. 1 FTU = 1 NTU.

Organic contaminants may be natural in origin, such as humic substances, or may be various waste products from society. The concentration of organic contaminants is analysed by measuring the **C**hemical **O**xygen **D**emand, COD_{Mn} which is expressed in mg O_2/l.

In older standards the concentration of organic contaminants is expressed as a "permanganate value" or in mg $KMnO_4$/l, where 1 mg COD_{Mn}/l is equivalent to about 4 mg $KMnO_4$/l. Another method is to determine the concentration of **T**otal **O**rganic **C**arbon, which is known as a TOC analysis.

As a result of more sophisticated in analytical methods in recent years we have become aware of a growing number of organic environmental toxins that biodegrade very slowly, such as PCBs, dioxins, pesticides and phenolic compounds, as well as halogenated organic compounds that can be formed during disinfection.

Bacteria and **viruses**. Measured as number/ml. Normally we analyse for the presence of coliform bacteria since these indicate whether there is a risk of pathogenic (disease-causing) bacteria and viruses.

Parasites and **amoebae**. Parasitic single-celled organisms (protozoa) that can cause illness in man and animals.

In recent years the presence of Cryptosporidium and Giardia has been identified following serious outbreaks of gastrointestinal infections that were previously unexplained. Cryptosporidium and Giardia are highly resistant to disinfection with chlorine.

The treatment method used for the undesirable substances listed above is chemical precipitation, which makes them easy to remove.

Corrosion is a problem that must be considered during water treatment. Water can behave in a corrosive manner that leads to a reduction in the quality of water. Depending on the composition of the distribution piping a variety of substances, including copper and iron, can be dissolved and contaminate the water. During water treatment it is important to produce water of a quality that gives the least possible corrosion problems. There are several factors that affect corrosion: pH, alkalinity, calcium concentration, presence of disinfectants, concentrations of inorganic salts and organic compounds. There are three main parameters that influence corrosion and which must be controlled: pH, alkalinity and calcium concentration. Plastic piping is not affected by pH and alkalinity, but can cause bacterial growth in distribution pipes due to a biological film that grows on the inside of the pipes.

Different countries have drawn up different recommendations in order to produce potable water that causes the minimum acceptable corrosion risk. There are large variations between these recommendations and it is probable that the dominant water chemistry in each country has influenced the values.

➤ **Table 2:2** Water that is acceptable from the corrosion viewpoint; recommendations for different countries.

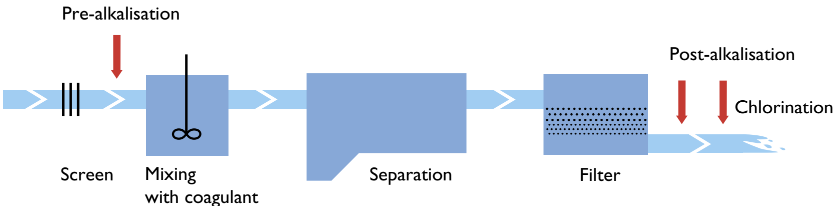
Source: VA-Forsk report, 1997-7, "Dricksvatten och korrosion – en handbok för vattenverken" (Potable water and corrosion – A handbook for waterworks)

	pH	Alkalinity mg HCO_3^-/l	Calcium mg/l	Chloride mg/l	Sulphate mg/l	COD_{Mn} mg O_2/l
Sweden	7,5-9	>60	20-60	<100	<100	<2
Norway	7,5-8,5	36-60	15-25	<25	<25	<2
Denmark	7-8	>100	20-200	<50	<50	<1,5
Finland	7,5-8,8	>36	<100	<25	<50	<2
Holland	7,8-8,3	>120	<150	<150	<100	-
Germany	6,5-9,5	-	<400	<250	<250	<5
England	5,5-9,5	>30	>60	<400	<250	-
USA	6,5-8,5	-	-	<250	<250	-
EU	6,5-9,5	-	-	-	<250	<5

Flockning.

Chemical treatment of surface water

The chemical treatment of surface water may follow the path outlined in figure 2:1. Several process stages may be added or removed, depending on the quality of the raw water.



➤ **Figure 2:1** Chemical treatment of surface water.

- **Mechanical separation**, designed to remove larger contaminants.

- **Pre-alkalisation**, designed to establish the optimum pH for the precipitation process. This stage is omitted in some waterworks, with the result that optimum conditions may be difficult to achieve in the chemical floccing stage. This can be compensated for to some extent through the choice of coagulant.

- During coagulation in the **chemical coagulation stage** aluminium salts and polyaluminium salts or iron (III) salts are used as coagulants.

Waterworks sometimes use a coagulant aid. Activated silicic acid (water glass) and polyelectrolytes are the most common choices.

- During the **separation stage** the flocs are separated from the treated water by **sedimentation** or flotation. Most of the precipitated contaminants are removed at this stage.

During sedimentation the flocs are separated by allowing them to settle to the bottom of a sedimentation basin. This happens because the flocs have a higher density than water and therefore tend to sink. The normal surface load in a sedimentation basin is around 1 m/h.

During flotation air bubbles become attached to the floc, which then floats up and creates a sludge layer on the surface. Air is dissolved in water at high pressure to create what is known as dispersion water. When the pressure is reduced to atmospheric pressure it results in the formation of microscopic air bubbles that stick to the flocs. This gives them a buoyancy that exceeds the sedimentation forces, so they rise to the surface. A flotation plant can be made more compact since the surface load in a flotation basin can be around 5–10 m/h. The sludge from a flotation plant often has a higher dry content than that from a sedimentation plant.

Långsamfilter.

In **direct filtration** a coagulant is added just before the raw water reaches the filter. Floc formation takes place in the filter bed, where the flocs are also separated. The coagulation time is considerably shorter (a few minutes) than with conventional coagulation (20–60 minutes). It is preferable to use a coagulant that is able to form flocs quickly, such as polyaluminium chloride.

- The **rapid sand filter** separates the remaining flocs, i.e. those flocs that were not trapped during the separation stage. A rapid filter has a filtration rate of 5–10 m/h.

- **Post-alkalisation** and **disinfection** are respectively designed to protect the distribution piping from corrosion and prevent bacterial growth.

Other effective methods of treatment are to supplement the process with **slow filtration**, **infiltration** or **activated carbon**.

Slow filtration depends on the formation of a biologically active layer that breaks down the remaining organic substances. This reduces the colour of the water and the chemical oxygen demand, while also reducing its taste and odour. A slow filter has a filtration rate of < 0,3 m/h.

Infiltration involves passing the surface water very slowly (over a period of days or months) through layers of sand and soil. This leads to separation of suspended solids and the breakdown of organic substances. The water is then pumped back up through the bed. The water quality is similar to that of groundwater, i.e. it has a low uniform temperature, reduced odour and taste, as well as a low concentration of organic substances. Prior to infiltration the water should be treated to reduce the concentration of suspended and organic matter.

In some cases chemical precipitation is carried out as a preliminary stage before the water goes to the infiltration stage. This is done to prevent this area from being clogged by particulate contaminants, and to ensure there is sufficient oxygen to break down organic matter in the filter bed. If there is a shortage of oxygen in the filter bed there is a risk of hydrogen sulphide formation and elevated levels of iron and manganese.

A reduction in COD_{Mn} by around 80% is reasonable.

The advantages of infiltration are that the technique is relatively inexpensive and requires only small amounts of chemicals. The filtration rate of an infiltration bed is around 0,1–0,2 m/h.

Water can also be treated with activated carbon if odour and taste are serious problems. This treatment can also remove environmental toxins from the water. The carbon can be added in powder form (PAC, Powdered Activated Carbon) at the time of precipitation, or alternatively the water can be passed through a fast filter containing Granulated Activated Carbon (GAC). The carbon in the filter must be replaced or reactivated at regular intervals, usually after one to three years in order to remain effective. The lower the contaminant load on the filter, the less often it requires reactivation.

Chemical precipitation of surface water

The purpose of chemical precipitation is to encourage humus and particles to coagulate and form flocs that can then be separated. The choice of coagulant is important to achieve the optimum coagulation and sedimentation characteristics. There is a comprehensive selection of coagulants available on the market today with various special characteristics to optimise the precipitation process.

There are two main mechanisms involved in chemical precipitation:

- **Charge neutralisation**. The net charge on the surface of the particles is negative. When positive aluminium or iron ions are added they neutralise the charge on the particles. This happens very quickly, in just 0,01–1 second. To provide optimum conditions the pH of the water should be between 4,2–5,2 for aluminium sulphate. For iron-based products the range is somewhat narrower.

- **Sweep coagulation**. In this phase of floc formation the particles are bound to the resulting metal hydroxide (aluminium or iron hydroxide) and adsorption takes place. This reaction is a little slower than charge neutralisation. It occurs within 1–7 seconds, and the pH should be between 5,5–6,5 for aluminium sulphate. For iron-based products the range is somewhat wider, around 5,5–8.

The reaction that waterworks should be primarily interested in is sweep coagulation, partly because it is often difficult to achieve the rapid and thorough mixing that is required for charge neutralisation, and partly because the pH during the precipitation stage is usually in the range pH 5,5–7,5.

What happens when the coagulants are added?

When an acidic substance (such as an acid) is added to water it raises the concentration of hydrogen ions, H^+, which causes the pH to drop. If the water contains ions that have the ability to neutralise the added hydrogen ions then the pH will not drop as much. Ions of this type are commonly present in water. They include hydrogen carbonates, carbonates, hydroxides, etc. These ions are said to have a **buffering** ability.

One measure of this buffering ability is known as the **alkalinity** of water and is usually given as "mg HCO_3^-/l water" or "milli-equivalents of acid/l". The ions that make the greatest contribution to the alkalinity of water are hydrogen carbonates and carbonates.

The following reaction takes place during chemical precipitation with Kemwater ALG, aluminium sulphate:

$$Al_2(SO_4)_3 + 6HCO_2^- \rightarrow 2Al(OH)_3 + 6CO_2 + 3SO_2^{2-}$$

The aluminium sulphate reacts with hydrogen carbonate, etc., to form aluminium hydroxide.

It can be seen from this formula that alkalinity (the hydrogen carbonate concentration) decreases and carbon dioxide increases. Both these changes lead to a reduction in pH. At the same time the water receives an excess of sulphate ions. Special measures must be taken to restore the alkalinity and raise the pH, such as adding lime in the form of limestone or slaked lime.

In PAX products the aluminium ions are polymerised and have a higher charge than the individual aluminium ions (Al^{3+}) in aluminium sulphate, for example, so the charge on the particles is neutralised more effectively (see chapter 7). The equivalent reaction for PAX with an OH/Al ratio of 1,5 (i.e. 1,5 moles of OH^- for each mole of Al^{3+}, or 50% basicity) proceeds as follows:

$$2Al(OH)_{1,5}Cl_{1,5} + 3HCO_3^- \rightarrow 2Al(OH)_3 + 3CO_2 + 3Cl^-$$

When coagulants, such as salts of aluminium or iron, are added to surface water they bind contaminants such as bacteria, colouring agents and other substances that cause turbidity to themselves, producing potable water that is clean and clear.

The reduction in alkalinity is lower and less carbon dioxide is produced.

If we compare the two reactions in terms of producing **1 mole of $Al(OH)_3$** we see the following:

➤ **Table 2:3** Comparison between the number of moles of aluminium sulphate and PAX needed to produce 1 mole of $Al(OH)_3$.

	Aluminium sulphate	PAX
HCO_3^- required	3	1,5
CO_2 produced	3	1,5
Increase in SO_4^{2-}	1,5	0
Increase in Cl^-	0	1,5

The difference is even greater if we choose a PAX product with a higher basicity, such as a Kemwater PAX-XL.

The higher the charge a product has, the smaller the reduction in alkalinity compared with a standard product. This reduces or even eliminates the need to add alkali in the form of lime or lye.

Water hardness

The hardness of water and its interaction with carbon dioxide play a central role in the chemistry of water. Hardness depends primarily on the presence of calcium (Ca) and magnesium (Mg). Theoretically, strontium (Sr) and barium (Ba) also contribute to the hardness of water, but these two elements generally occur in such low concentrations that they can be neglected for practical purposes. Hardness is usually expressed on the German hardness scale as °dH and is defined as:

1 °dH = 10 mg CaO / l

where the total calcium and magnesium content is calculated as calcium oxide, CaO.

Some countries use other definitions.

The lime – carbon dioxide equilibrium

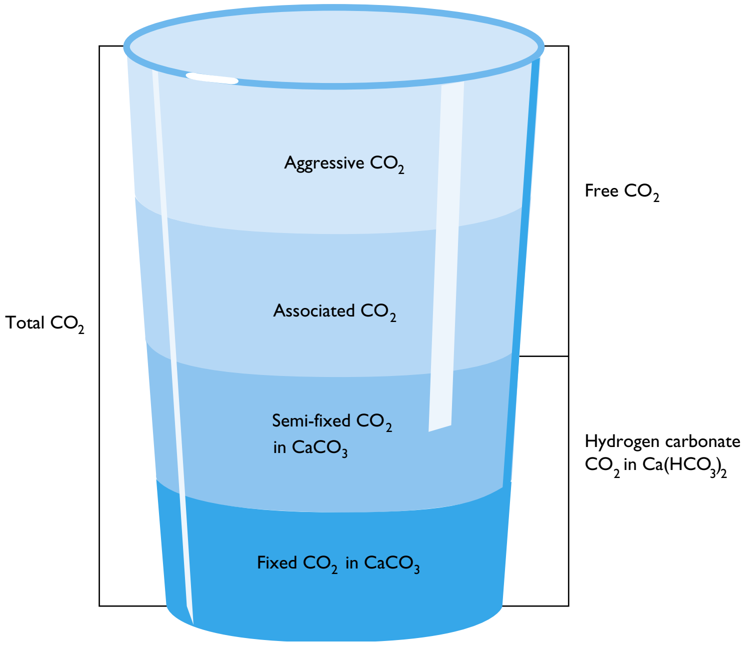
In its natural state water contains various amounts of dissolved substances. The one that has the most important effect on the properties of water is calcium hydrogen carbonate.

Calcium hydrogen carbonate does not exist in solid form, but is found in aqueous solutions in an unstable state, which is governed by the equilibrium reaction:

Ca^{2+}	$+$	$2HCO_3^-$	$\leftrightarrow$	$CaCO_3$	$+$	H_2O	$+$	CO_2
calcium ion		hydrogen carbonate ion		calcium carbonate, solid				carbon dioxide (to air)

Calcium carbonate, sometimes known as boiler scale, can be deposited in cooking pots and hot water heaters if calcium carbonate and carbon dioxide, CO_2, are not in equilibrium.

The favoured direction of this equilibrium reaction determines the properties of water in terms of aggressivity (corrosiveness) and lime precipitation. The temperature is also critical to this equilibrium reaction. Water that is in equilibrium at room temperature may precipitate lime when it is heated.



➤ **Figure 2:2** The various states of carbon dioxide in water.

To prevent the precipitation of calcium carbonate, $CaCO_3$, the water must have a certain concentration of **free CO_2**. This is usually referred to as the **associated CO_2**. If the water contains a higher concentration of free CO_2 than is required to keep calcium and hydrogen carbonate in solution then the excess concentration is referred to as **aggressive CO_2**. This makes the water corrosive. If the water contains a lower concentration of **free CO_2** than **associated CO_2** then calcium carbonate will precipitate. This can lead to the blockage of distribution piping and deposits on heated surfaces (boiler scale).

The **total concentration of carbon dioxide** in water can be divided into two main components, **free carbon dioxide** as described above, and **hydrogen carbonate carbon dioxide** (bicarbonate carbon dioxide).

In the past, the **hydrogen carbonate carbon dioxide** was further divided to distinguish between the CO_2 that is dissolved in water in the form of hydrogen carbonate (**semi-fixed CO_2**) and the carbon dioxide that originally came from the calcium carbonate that dissolved to form hydrogen carbonate (**fixed CO_2**).

The various states of CO_2 in water are shown schematically in figure 2:2.

Calculating the precise theoretical equilibrium state is difficult since the required equilibrium constants, dissociation constants and solubility products all depend on the temperature and total concentrations of other ions in the water. This means, for example, that water that is in equilibrium at the waterworks could later precipitate calcium carbonate on a warm surface, such as a heat exchanger.

Various attempts have been made to simplify these calculations graphically. Of the many diagrams that can be found in the literature it is worth mentioning Tillman's curve, Langelier's diagram and Hoover's nomogram, which are among the most commonly used.

Nowadays there are also simple PC programs for carrying out these calculations.

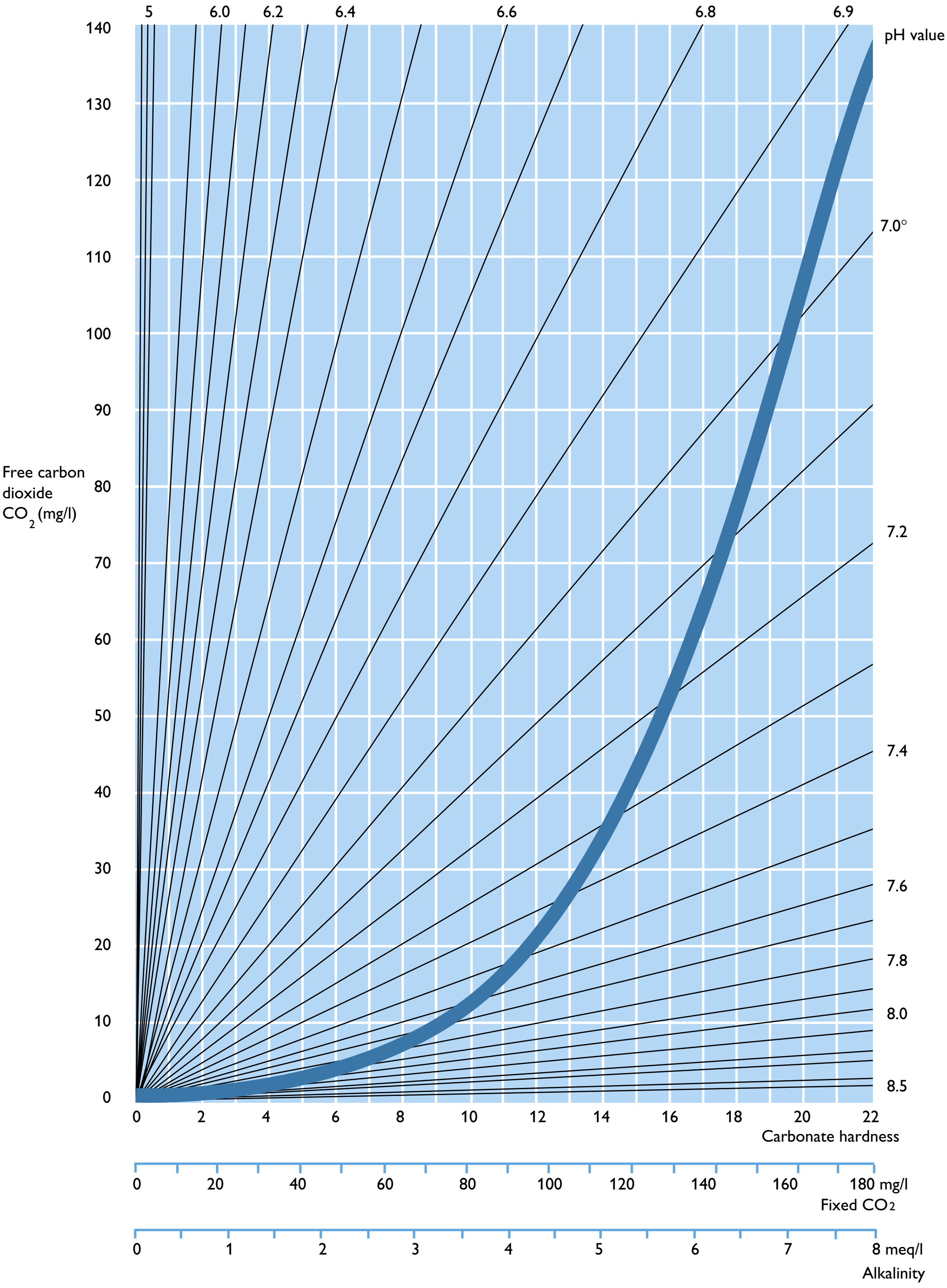
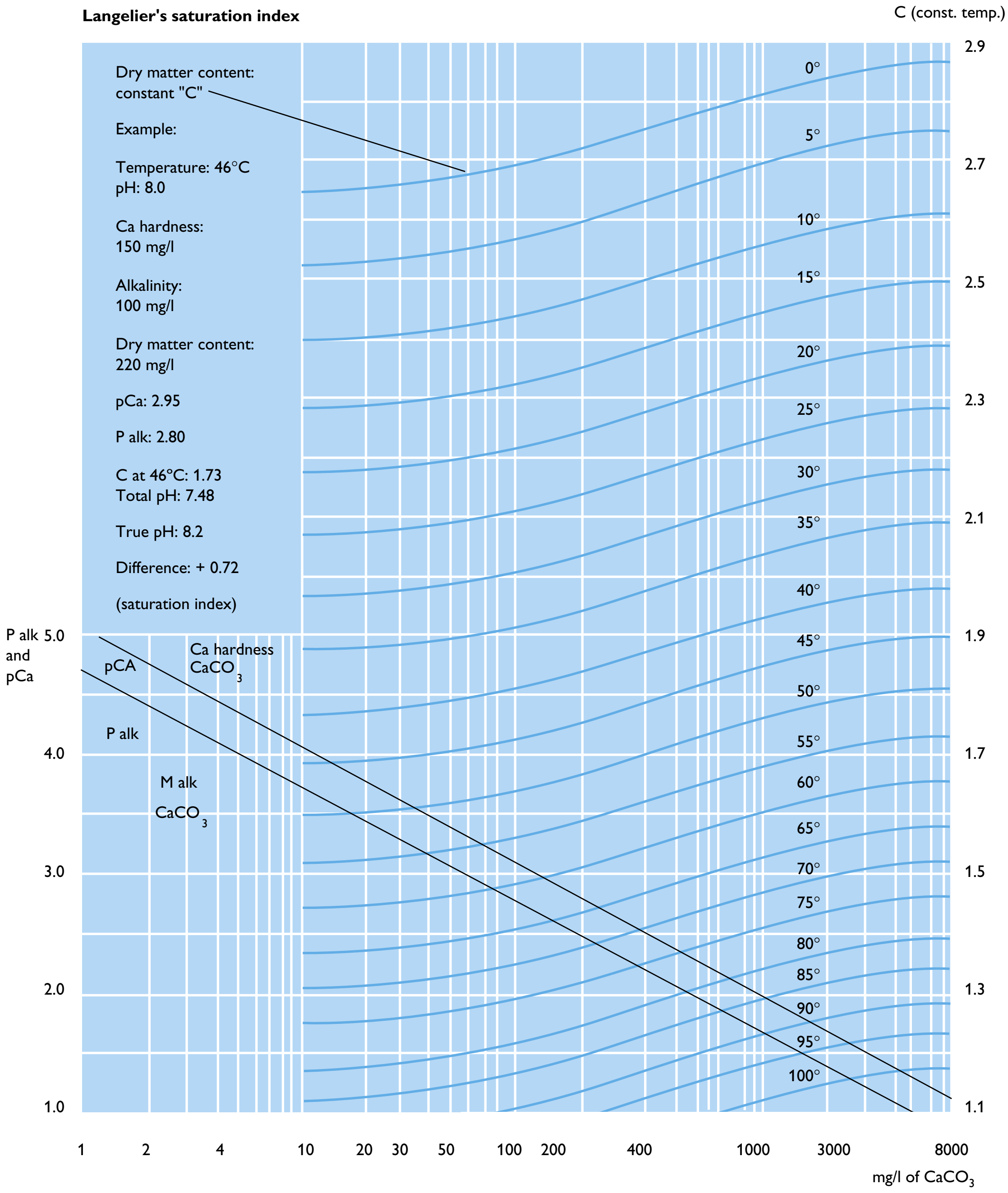
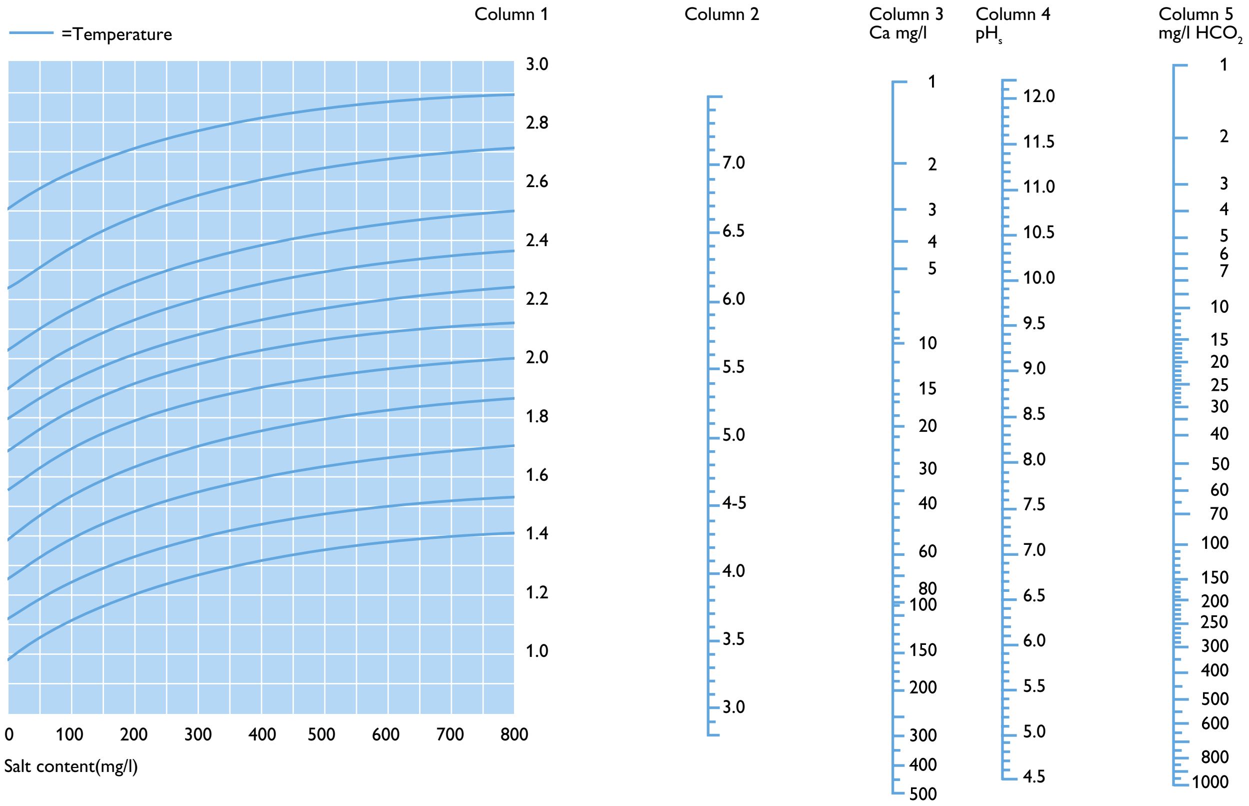


Figure 2:3 Tillman's curve.



➤ **Figure 2:4** Langelier’s diagram.



➤ **Figure 2:5 Figure 2:5** Hoover’s nomogram.

The infection is spread by contact between people, and between animals and people, as well as indirectly through contaminated water.

Cryptosporidium and Giardia

In recent years greater attention has been given to the causes of outbreaks of illness that have occurred in the US, for instance, as a result of distributing infected water to consumers. One example is the Milwaukee outbreak in 1993, when more than 400,000 people suffered from diarrhoea after drinking municipal water. The cause of this outbreak was a parasitic protozoan (single-celled organism) called Cryptosporidium. In the dormant state these protozoa are surrounded by protective shells known as oocysts (Cryptosporidium) and cysts (Giardia) that effectively shield them from chlorine disinfection.

The symptoms are stomach cramps, diarrhoea and fever. The infection is spread by contact between people, and between animals and people, as well as indirectly through contaminated water. The infectious dose is low, requiring just 10–100 Cryptosporidium oocysts to cause illness in one person. In the case of Giardia it only takes between 25 and 100 cysts, which means that anything other than very low concentrations cannot be accepted in potable water.

Several species of Cryptosporidium and Giardia are known, but it is only Cryptosporidium parvum and Giardia intestinalis that are known to cause such progressions of illness in people. These organisms are found in surface water, such as lakes and rivers.

Oocysts are extremely small, measuring 3 to 5 µm, while cysts are somewhat larger, at 11 to 14 µm. They can be removed by effective chemical precipitation and filtration, or microfiltration (a form of membrane filtration). Because protozoa behave like particles a coagulant should be chosen that is particularly effective at particle reduction.

The Swedish National Food Adminstration, SLV, and the Swedish Institute for Infectious Disease Control, SMI, have jointly investigated the occurrence of these two protozoa in Swedish surface water sources. The investigation was carried out at 26 surface waterworks in 21 municipalities, focusing particularly on water sources that were affected by agriculture or sewage. The investigation was carried out in autumn 1996 and spring 1997. It turned out that 38% of the raw water samples that were examined contained Cryptosporidium and/or Giardia. The investigation also showed the presence of Cryptosporidium in a potable water sample.

Bottled water

The range of bottled water is large and growing all the time.

Waterworks in industrialised countries can usually supply residents with very high quality tap water. The quality of tap water is regulated by EU directive 98/83/EEC. Bottled water is regulated by EU directive 80/777/EEC.

The range of bottled water is large. However, all the brands are not as "natural" as the consumer may be led to believe. Some of the "table water" on the market is common tap water, possibly filtered through a carbon filter to remove any taste of chlorine.

Under EU directives bottled water can be divided into various categories:

Natural mineral water

This water must come from an underground spring and be bottled on site. It must not contain any additives other than carbon dioxide and may not contain more than 500 mg of mineral salts per litre.

Spring water

This water must come from an underground spring but has no specified maximum content of mineral salts.

Other water

Water that does not meet the requirements of the above categories. Carbon dioxide, aroma enhancers and mineral salts may be added. "Other water" covers all potable water, including municipal tap water.

Private wells

Many private wells may contain acidic or acidified water, which causes a variety of problems. These may be problems of health or of a technical nature. Examples include high concentrations of aluminium and copper, corrosion to pipes and pitting corrosion.

In order to remedy these problems the pH must be raised to a suitable level. This can be done by passing the water through a filter containing limestone or dolomite.

Many private wells may contain acidic or acidified water that causes problems of various types.

Other risks that should be considered when using wells include poorly fitting well covers, penetration of water from pipe trenches and connecting pipes, the risk of contamination through ventilation pipes (lack of insect traps), sludge that can collect at the bottom of the well, and contamination by traces of pesticides. High nitrate concentrations in well water can be a sign of the presence of pesticide contamination (leakage from agricultural land).

Pesticide traces

Another problem that is attracting growing concern is the presence of organic compounds from pesticides that are spread on agricultural land, sometimes in an uncontrolled manner. These substances biodegrade very slowly and cause major problems due to their high toxicity to people and animals.

Pesticides is the collective name for "growth modifying" organic substances that are used to prevent undesirable organisms (such as plants, insects, algae and fungi) from damaging crops. The contamination of groundwater has taken place primarily over the last 40 years. The following techniques can be used to remove pesticides:

- **Separation by adsorption on activated carbon.**
- **Breakdown by oxidation (using ozone, hydrogen peroxide or chlorine).**
- **Biological decomposition on the surface of activated carbon.**

Bildtext!?

Who is responsible for water quality?

Water is our most vital commodity. A whole range of international rules and national authorities has therefore been put in place to safeguard the quality of water. Here is a summary of the authorities and directives that govern potable water issues in the European Union.

EU regulations include a number of directives that govern water issues.

The surface water directive, 75/440/EEC, is designed to protect the lakes and waterways that are used as sources of raw water for producing potable water. This directive, which has been around for some time, has largely faded in importance since the arrival of the more recent potable water directive. The surface water directive will be incorporated in a **framework directive** that encompasses the protection of surface water and groundwater and which came into effect in the year 2000.

The groundwater directive, 80/68/EEC, aims to protect groundwater from contamination by harmful or hazardous substances. This directive will also be incorporated in the framework directive together with the surface water directive.

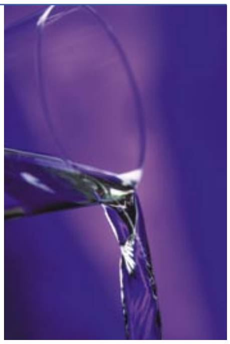
The potable water directive, 98/83/EC, is designed to safeguard the quality of water that is intended for use as potable water. In December 1998 the EU council adopted a revision of the directive that brought it in line with modern scientific understanding and simplified the text. It is interesting to note that the council permits the member states to enforce stricter threshold values than the directive itself gives. Some water quality parameters have been added and others removed, reducing the total to 50 from the previous 60. One of the more important changes from the previous version of the directive is that the threshold value for lead has been reduced from 50 µg/l to 10 µg/l. This considerable reduction in lead content could cause problems for some member states, since it will require major investments in the distribution network to meet the new requirements.

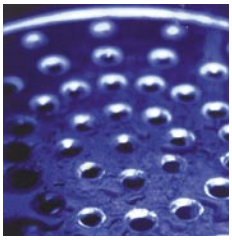
Chapter 3

Wastewater treatment

Chapter 3 Wastewater treatment

Wastewater treatment





Wastewater is not a new phenomenon. Every city throughout history has produced contaminated water. In older civilisations it was simply emptied onto the street, or at best led away into a ditch. As a result, diseases such as cholera spread easily through cities, and the stench must have been indescribable.

The problem of contaminated water was understood back in the time of the Romans. In around 400 BC the Romans laid the first sewer in Rome, known as the Cloaca Maxima. By taking away wastewater in a closed system they succeeded in improving the city environment. There are letters from that time that describe Rome as smelling as sweet as the mountains.

The treatment of wastewater is a more recent invention. The first places to introduce wastewater treatment were early industries, which could inflict severe local pollution on the recipient water. This began at the end of the nineteenth century, but it was not until around the 1930s that municipal wastewater treatment became more widespread. Initially the water was simply treated mechanically, but as the years passed and urbanisation increased, the treatment methods became more sophisticated. Today we can purify wastewater to any degree required; it is simply a matter of how much we are willing to pay and what requirements have to be met.

Although advanced wastewater treatment has only been developed in recent decades, we have understood the principles of mechanical, biological and chemical treatment for at least a hundred years. Since then, development has concentrated mainly on learning about the mechanisms and how the various techniques can be combined. With today's state of knowledge of the different water treatment processes we can combine the best of several worlds and treat wastewater efficiently.

"It isn't pollution that's harming the environment. It's the impurities in our air and water that are doing it."

Dan Quayle

80–90% of the nitrogen in wastewater comes from urine.

The nature and composition of wastewater

Contaminants

Wastewater contains most of the substances found in our society. These can be divided into:

- **suspended matter**
- **oxygen-demanding substances**
- **nutrient salts**
- **bacteria**
- **viruses**
- **parasite spores**
- **heavy metals**
- **environmentally harmful substances**

These contaminants can be classified on the basis of particle size into dissolved, colloidal, suspended and sedimentary contaminants. In order to choose the most suitable treatment process it is very important to know particle size as well as the composition of wastewater.

➤ **Table 3:1** Definition of particle sizes.

	Dissolved	Colloidal	Suspended	Sedimentary suspended
Particle size, μm	< 0,1	0,1–1,0	1–100	> 100

Another way of classifying contaminants is to divide them into organic and inorganic matter. The organic contaminants generally comprise around one-third each of dissolved, colloidal and suspended solids. The inorganic material mainly comprises dissolved substances.

Organic contaminants

The most common method of measuring the degree of contamination is to give the total content of organic contaminants per unit volume of wastewater. However, very few studies have attempted to classify the organic substances in municipal wastewater in detail. Table 3:2 shows the decomposition of organic substances as determined by the HYPRO project[1].

On average, a drop of water spends 4000 years in the ocean. But once that water has evaporated and become part of the atmosphere it takes just 10 days until it rains on to the sea or land.

➤ **Table 3:2** Organic constituents of municipal wastewater.

Substance	Percentage organic carbon in wastewater
Carbohydrates	11–18%
Proteins	8–10%
Free amino acids	0,5–1,5%
Higher fatty acids	23–25%
Soluble organic acids	7–11%
Esterified fatty acids (fat)	9–12%
Surfactants	4–6%
Others	25–28%

The concentration of organic substances is usually measured as:

- biochemical oxygen demand (BOD)
- chemical oxygen demand (COD)
- loss on ignition (LOI)
- total organic carbon (TOC)

Biochemical Oxygen Demand (BOD) is a measure of the concentration of biodegradable substances in the wastewater. These substances are broken down by bacteria, which consume oxygen. To determine the oxygen demand we measure the amount of oxygen the micro organisms use over a period of 5 days (BOD_5) or 7 days (BOD_7) to break down the organic contaminants in water at a temperature of 20°C. BOD is measured in units of mg oxygen/l or g oxygen/m^3.

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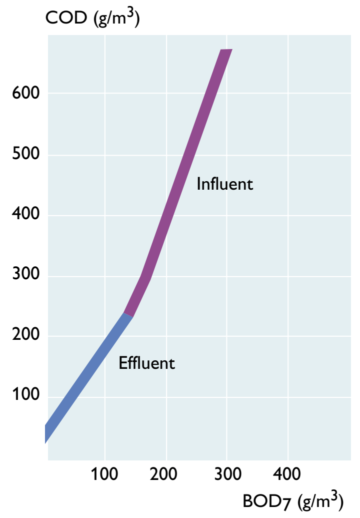
[1] A EUREKA project in which Kemwater took part. The aim of the project was to produce a source of carbon for nitrogen removal from sludge.

The following relationship applies to municipal wastewater:

$$BOD_7 = 1{,}15 \times BOD_5$$

Ammonium is an oxygen-demanding substance, since oxygen is used to oxidise the nitrogen in the ammonium ion to form nitrate. This process uses 4,5 grams of oxygen for every gram of nitrogen.

Microbiological analyses determine the concentrations of bacteria, viruses and parasite spores. These analyses can be carried out on both influent (untreated) and effluent (treated) wastewater, and are expressed as a number per 100 millilitres.



➤ **Figure 3:1** Example of the relationship between BOD_7 and COD.

Chemical Oxygen Demand (COD) is a measure of the concentration of contaminants in the water that can be oxidised by a chemical oxidising agent. The reaction time is considerably faster than the analysis of BOD. Complete oxidation is usually achieved by using potassium dichromate or potassium permanganate at high temperature in strongly acidic solutions. The amount of oxidising agent required is a measure of the organic content and is converted into the equivalent oxygen concentration, so values are given in mg oxygen/l or g oxygen/m^3.

The relationship between BOD and COD may appear as in figure 3:1. The ratio between COD/BOD indicates the degree of biodegradability of the wastewater. Low values, i.e. COD/BOD <2, indicate matter that biodegrades relatively easily, while high values indicate that the material will biodegrade very slowly. This relationship cannot be applied generally, but must be determined for each source of wastewater, since there can be major variations depending on the composition of the wastewater. In the case of untreated municipal wastewater the COD/BOD ratio is however usually around 2–3, while the ratio for treated wastewater may be higher than 4.

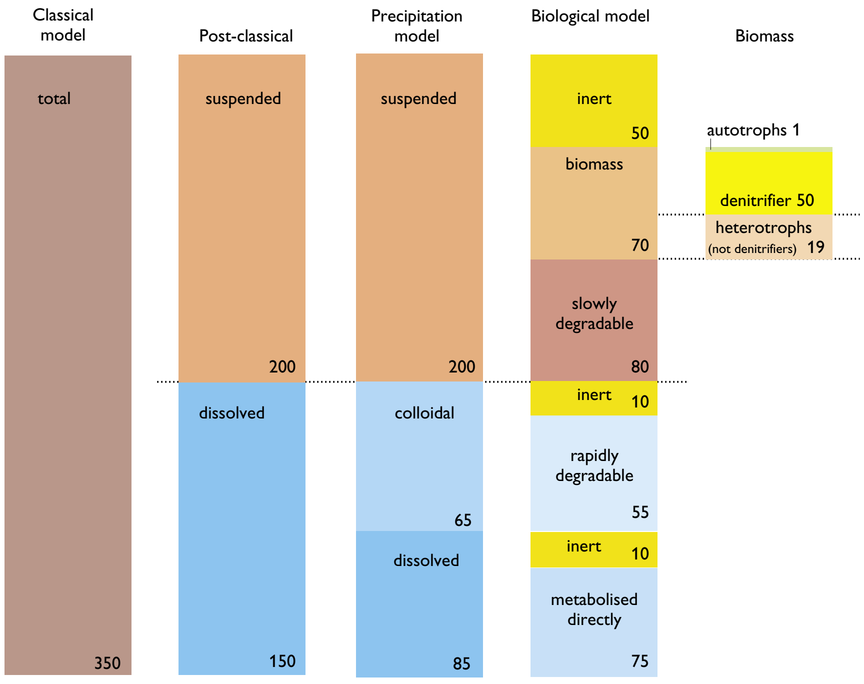
Loss on ignition (LOI) is defined as the percentage weight change in a dry substance when a sample is ignited, i.e. heated to 550°C (Swedish Standard).

Total organic carbon (TOC) is a measure of the content of organic matter, which is determined by measuring the amount of carbon dioxide generated by burning a sample. It is measured in mg C/l.

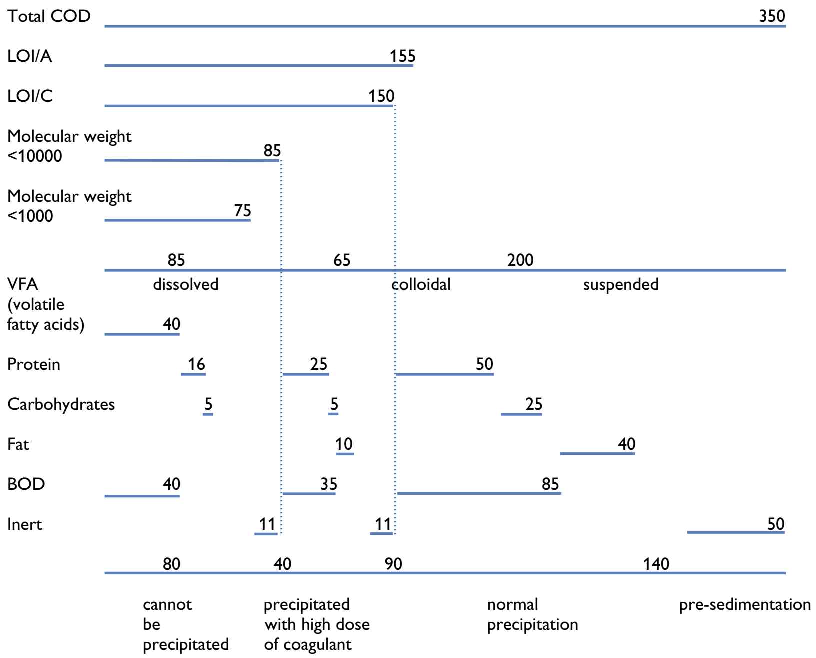
New analytical methods have made it possible to determine the levels of organic toxins, or environmentally harmful substances, more accurately. This means that some completely new expressions will be introduced in the future. These include chlorinated hydrocarbons. The following terms are used as measures of chlorinated hydrocarbons:

TOX = Total Organic Halides
AOX = Absorbable Organic Halides

However, the concentrations of organic environmental toxins are often very low, which means that these analyses have their limitations. Organic environmental toxins can become concentrated in the sludge that is removed from the treatment process. These can include PCBs, toluene, nonyl phenol and PAH. Analyses for these substances are therefore carried out on the sludge.



➤ **Figure 3:2** COD distribution in wastewater, g COD/m^3.



➤ **Figure 3:3** COD distribution in wastewater, according to HYPRO method, g COD/m^3.

It is also possible to divide COD into substances that are biodegradable and how quickly they are broken down. The composition of wastewater can also be classified according to particle size, volatile fatty acids (VFA), proteins, etc., as shown in figure 3:3.

The HYPRO method

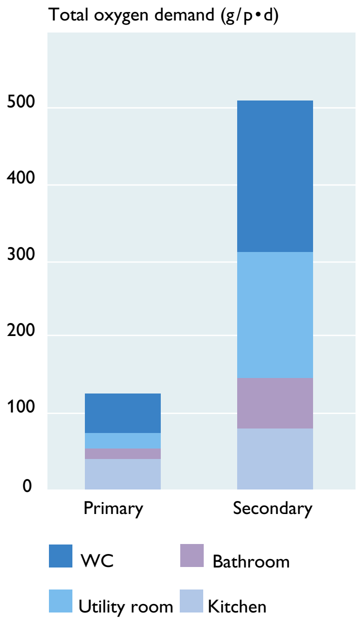
In the Hypro process, biodegradable organic substances are removed by pre-precipitation in order to reduce the load on the subsequent biological process. The organic compounds that are removed are hydrolysed to make them readily biodegradable, and then returned to the treatment process as a source of carbon. In order to choose the most appropriate treatment process, the wastewater should first be classified into more detailed constituents than COD and BOD, since these classifications are far too coarse. They are excellent for recipient control, but not for operation or selection of a treatment process. In biological processes especially, the oxygen and nitrate respiration rates of these organic compounds (COD and BOD) are highly significant.

Inorganic substances

The inorganic constituents of wastewater consist mainly of dissolved salts and are determined largely by the ion composition and the salt content of the tap water. There is not normally any need to remove these salts however. Current treatment processes concentrate on reducing the content of suspended solids, (SS), organic substances (COD, BOD), phosphorus (P), nitrogen (N) and heavy metals. Effective reduction of suspended solids also means the effective reduction of bacteria, viruses and other particles that can cause infection.

Heavy metals are separated with the sludge.

Nitrogen and phosphorus are nutrient salts, i.e. they provide fertilising nutrients that encourage the growth of organic matter, such as algae, in recipient water. This growth can cause secondary production of organic matter and lead to a considerably higher oxygen demand than that due to the primary organic contaminants in wastewater. See figure 3:4.



➤ **Figure 3:4** Primary and secondary oxygen demand.

1 gram of nitrogen can give rise to around 14 grams of secondary oxygen-demanding organic matter.

1 gram of phosphorus can give rise to around 100 grams of secondary oxygen-demanding organic matter.

Phosphorus

Phosphorus occurs in wastewater partly as organically bonded phosphorus, and partly as inorganic phosphorus in the form of polyphosphate and orthophosphate. Organic phosphorus is mainly bonded to solid particles, while polyphosphate and orthophosphate occur mainly in dissolved form.

In a biological treatment process phosphorus is hydrolysed to form orthophosphate, which is the type of phosphorus that plants can absorb most easily.

$$H_3PO_4 \quad \leftrightarrow \quad H_2PO_4^{-} \quad \leftrightarrow \quad H_2PO_4^{2-} \quad \leftrightarrow \quad PO_4^{3-}$$

phosphoric acid — ortho phosphate ion

Removing phosphorus from detergents does not solve the problem of secondary production of organic matter.

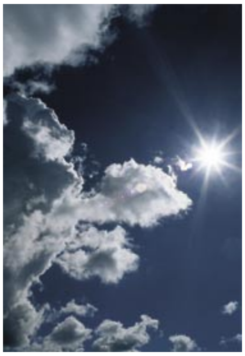
The major sources of phosphate are phosphate detergents and human waste. The use of phosphorus in detergents has been widely discussed in recent years, since around 30% of the phosphorus content in wastewater comes from detergents. Removing phosphorus from detergents would however only slightly alleviate the problems caused by secondary production of organic matter (algal growth), because ultimately it is the concentration released by the treatment plant that causes the problems. The solution to this problem is to efficiently reduce the concentration of phosphorus when treating wastewater.

The phosphorus concentration is given either as mg/l of total phosphorus (P_{tot}) or mg/l of phosphorus as phosphate (PO_4^{3-}-P).

Instead of using P, the concentration of phosphorus is sometimes given as PO_4^{3-} or P_2O_5. Conversion factors are given in table 3:3.

➤ **Table 3:3** Conversion factors for total phosphorus.

P	PO_4^{3-}	P_2O_5
1	3,06	2,29
0,33	1	0,75
0,44	1,34	1



Nitrogen is the seventh most abundant element in the universe. It is present in the sun, the stars and interstellar dust. On Earth, there is nitrogen in the atmosphere, the Earth’s crust, the hydrosphere and the biosphere. Dry air contains 78,08 percent nitrogen by volume, or around 75,5 nitrogen by weight.

Nitrogen

Nitrogen occurs in wastewater partly as organically bonded nitrogen, and partly as inorganic nitrogen in the form of ammonium (NH_4^+), nitrite (NO_2^-) and nitrate (NO_3^-).

The concentration of nitrogen is given as total nitrogen in mg/l. This is the sum of organic nitrogen and nitrogen in the form of ammonium, nitrite and nitrate. The concentration of nitrogen can also be expressed as Kjeldahl nitrogen, which is the sum of organic nitrogen and nitrogen from ammonium.

As well as being a nutrient for algal growth, nitrogen in the form of ammonium is also a cause of oxygen demand, since nitrogen-oxidising bacteria use large amounts of oxygen to convert ammonium to nitrate. This oxidation process is called nitrification. During nitrification, the oxygen consumption is almost five times the concentration of nitrogen that is present as ammonium, and is roughly the same as the oxygen consumption for oxidising organic matter in the wastewater. Effective treatment of oxygen-demanding substances therefore also requires nitrification.

Other contamination parameters

Total solids (TS) is another measure of the total concentration of contaminants in wastewater and is therefore the sum of solid and dissolved substances. TS is expressed in mg/l.

Suspended solids (SS) is a measure of the concentration of solid particles in wastewater and is also expressed in mg/l.

Contamination levels in wastewater show large variations between different locations depending on the type of local industry and the leakage of ground water.

Table 3:4 shows approximate typical contaminant concentrations in municipal wastewater, expressed in grams per person equivalent per day (g/person/day).

➤ **Table 3:4** Typical contaminant concentrations in municipal wastewater.

Contaminants	g/p•d
Chemical oxygen demand (COD)	120–180
Biochemical oxygen demand (BOD_7)	60–90
Phosphorus (P)*	2,0–3,5
Nitrogen (N)	10–14
Suspended solids (SS)	70–90
Total solids (TS)	150–250

*Note: phosphorus levels may be lower in many countries where phosphate-free detergents are used.

The quantities in the table above are often expressed as person equivalents (pe). Contaminants from industry are often also expressed in person equivalents.

The water consumption of an average household in industrialised countries is around 200 l per person per day. The amount of wastewater that reaches a treatment plant can be as much as twice this figure due to surface water and ground water that leak into the system.

A rule of thumb that can be used for municipal wastewater is that BOD_7 and SS are almost always the same – for both untreated and treated wastewater.

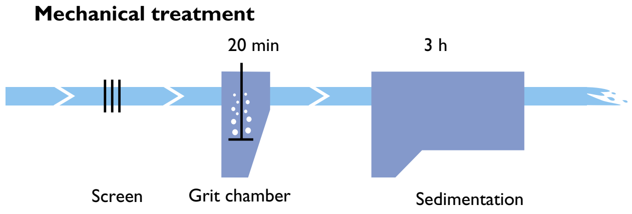
➤ **Table 3:5** Average contaminant concentrations for wastewater of 400 l/pe/d. Values vary greatly over a 24-hour period.

Contaminant concentration	mg/l
Suspended solids (SS)	200
Biochemical oxygen demand (BOD_7)	200
Phosphorus (P)	7
Nitrogen (N)	30

Municipal wastewater treatment

Mechanical treatment

The simplest form of wastewater treatment is to remove the contaminants mechanically. Mechanical treatment is usually carried out in two stages. First the coarse contaminants are removed by means of screens and sand traps. The remaining suspended solids are allowed to sink to the bottom in a sedimentation basin. Using this method, around 50–60% of suspended solids and around 30% of BOD can be removed from wastewater.



➤ **Figure 3:5** Mechanical treatment stages.

The coarser contaminants, such as rags, twigs, scraps of food, etc., are separated mechanically by passing the water through screens. These treatment screens are coarse, with gaps ranging in width between 3 and 20 mm, which means that relatively large particles pass to the next treatment stage, the sand trap.

The heavier contaminants, such as sand, gravel and coffee grounds, sink to the bottom of the sand trap. The sand trap is designed specifically to separate the heavier particles. Often the sand trap is combined with some means of aeration to keep the water oxygenated (aerobic) and facilitate grease removal, as well as removing heavier particles. A sand trap normally has a retention time of around 20 minutes.

After the sand trap, the remaining suspended contaminants are allowed to settle in a larger sedimentation basin. This basin is charged with 1–3 m^3 of water per m^2 of basin area each hour, depending on the treatment process. In other words the basin has a surface load of 1–3 m/h.

surface load (m/h) = flow (m^3/h)/surface area (m^2)

The normal retention time for water in the basin is 2–3 hours.

Because mechanical treatment only removes around one-third of the oxygen-demanding contaminants (BOD) from the water, and only some of the contaminants containing nitrogen and phosphorus, this treatment method is generally inadequate by itself and should therefore only be regarded as a preliminary stage. The main benefit of mechanical treatment is to prevent the formation of sludge mounds around the outflow in the recipient waterway.

This treatment method has nevertheless been the dominant process around the world. It is simple, requires a small investment and is easy to operate. Despite everything, this process does clean water to some extent and is therefore better than no treatment at all. Mechanical treatment also forms the first stage of more sophisticated treatments and is known as primary treatment.

Mechanical treatment produces sludge quantities (primary sludge) of around 50–60 g SS/pd, which is thickened to a total solids (TS) content of 4–6%, which is equivalent to 0,8–1,5 l/pd.

Biological treatment

Biological treatment is normally the second treatment stage in a wastewater treatment plant and is therefore also known as secondary treatment. Usually the water is first treated mechanically (primary), and then undergoes a biological treatment stage that is designed to separate and break down organic contaminants with the aid of microorganisms. The contaminants are converted into a biological sludge (= cell mass).

In conventional biological treatment systems, organic matter is broken down. Only a small proportion of nutrient salts, such as nitrogen and phosphorus, are removed.

The decomposition cycle is a very complex process that consists of a long series of subsidiary reactions. The rate of decomposition depends on many factors. In addition to oxygen content, pH, microorganisms, temperature, contaminant type, toxic substances and treatment method, the particle size of the contaminants is also very important.

The contaminants in wastewater are primarily broken down by bacteria. These bacteria usually specialise in breaking down a specific substance or group of substances. As mentioned previously, wastewater contains a variety of different contaminants, which means that a number of different species are used in biological treatment. The above-mentioned factors, such as oxygen content, temperature, etc., also influence the combination of species that are chosen.

The bacteria that are used in biological treatment are not the same sort of bacteria we usually think of. They are not disease-causing (pathogenic) bacteria, but naturally occurring bacteria that are found in soil and water. In a biological treatment process these bacteria are simply brought together in large numbers to tackle the decomposition process in a limited space.

Biological treatment systems are normally designed to break down organic substances. Nutrient salts, such as nitrogen and phosphorus, are only marginally reduced in a normally loaded, conventional biological treatment system. Only the proportion of nitrogen and phosphorus that is assimilated (taken up) by the cell mass is removed. Usually we would expect this to be equivalent to a $BOD_5/N/P$ ratio of 100/5/1 based on the influent values. The TS content of this sludge, the excess sludge, would contain around 7–10% N and 1–3% P.

Treatment methods that are used to remove phosphorus and nitrogen are discussed under the section on Nutrient salt reduction.

A biological treatment process also contains other microorganisms in addition to bacteria. A variety of different higher-level species (protozoa and metazoa) are always present in the treatment process. Just like the various species of bacteria, these species carry out various tasks in the treatment process. Some live by eating particles and free-swimming bacteria (see activated sludge process). Others live on dead or living bacteria and organisms. There are worm-like organisms (oligochaetes) that tunnel through the biomass and improve water penetration and hence also treatment efficiency.

There is one thing these organisms all have in common. They aid the water treatment process and reduce sludge production. A well-cultivated fauna of protozoa and metazoa is a sign of an effective biological treatment process.

Three types of biological processes are used in wastewater treatment: **anaerobic**, **aerobic** and **anoxic** decomposition.


Bildtext?

Anaerobic decomposition

An anaerobic process occurs in the absence of oxygen or nitrate. When oxygen is not present in wastewater the contaminants are decomposed anaerobically. Organic substances are converted to methane, carbon dioxide and water. A small fraction of the organic matter is also converted into new biomass.

Anaerobic decomposition is normally only used for the treatment of heavily contaminated industrial wastewater, and as a general process for stabilising sludge, when it is known as **digestion**.

Anaerobic decomposition is considerably slower than aerobic processes. The bacteria cannot exploit the available "food" – the substrate – as effectively, and therefore grow more slowly. A large proportion of the food is used to produce energy, and only a small fraction to build up biomass. **One (1) kg of COD yields around 0,1 kg of biomass**. The rest is used to generate energy for the organism and produce methane gas, which has a high energy content.

To increase the decomposition rate in anaerobic decomposition the temperature of the sludge or water is usually increased. The temperature in a digester is normally around 35°C. Municipal wastewater in Nordic countries usually comes in at a temperature of between 5°and 20°C. This is too low a temperature for an anaerobic process to be considered suitable. Even in warmer parts of the world, where the average temperature is up to 25°C, anaerobic decomposition is still inadequate.

In the case of industrial wastewater, especially from the food industry, anaerobic processes can be very attractive as this water is sometimes at high temperature, is highly concentrated and has low flow rates.

Aerobic decomposition

This process, which takes place in the presence of oxygen, means that the microorganisms use oxygen in the water to oxidise organic matter and produce carbon dioxide and water, as well as biomass.

As mentioned above, the aerobic treatment process is considerably faster than the anaerobic process, thanks to the presence of oxygen. This means that the bacteria can make better use of the substrate and can create biomass more readily. **One (1) kg of COD yields around 0,5 kg of biomass**, while the rest is used to generate energy.

The aerobic process is also affected by temperature. Too low a temperature reduces the decomposition rate, but this can be compensated for by increasing the concentration of microorganisms. The aerobic treatment process can work well at temperatures down to 5°C and is considerably less sensitive than the anaerobic process.

When municipal wastewater is treated using the aerobic process the microorganisms may be made to grow on a solid carrier material in what are known as biofilm processes (immobilised cultures), or they may be freely suspended in the aqueous phase in the form of biological flocs, (suspended cultures).

Anoxic decomposition

The anoxic process is similar to the aerobic one, but in this case the bacteria "breathe" using oxygen obtained from nitrate, rather than using added oxygen. The decomposition process produces carbon dioxide, water and nitrogen gas. This process is therefore used for nitrogen reduction (see the chapter on Denitrification) since nitrogen is released from the water as gas. Anoxic decomposition is not as fast as the aerobic process but it is considerably faster than the anaerobic process.

This process will only work in the presence of organic substances (BOD/COD), since heterotrophic bacteria are unable to use carbon dioxide to build biomass. **One (1) kg of COD yields 0,5 kg of biomass**, i.e. the same quantity as aerobic processes. This process must be carried out in the absence of free oxygen, since the bacteria prefer to use oxygen than nitrate for respiration.

Immobilised and suspended bacterial cultures can also be used for anoxic treatment.

During anaerobic decomposition	**1 kg of COD yields 0,1 kg of biomass**
During aerobic decomposition	**1 kg of COD yields 0,5 kg of biomass**
During anoxic decomposition	**1 kg of COD yields 0,5 kg of biomass**

Suspended cultures

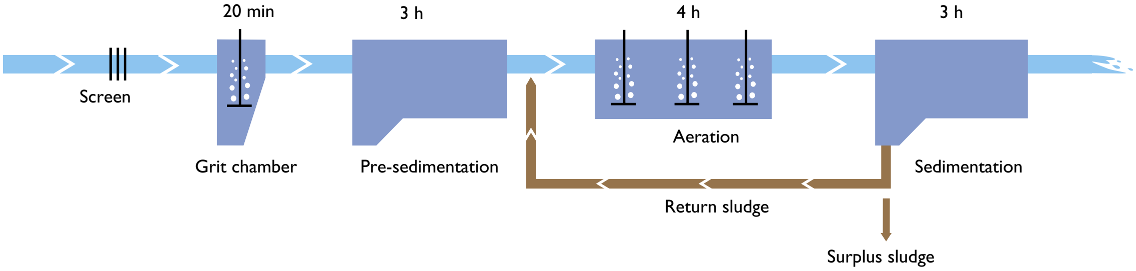
Activated sludge process

During treatment with activated sludge the biologically active microorganisms are suspended in sludge flocs in the wastewater. A sludge floc, or biofloc, consists mainly of a specific type of bacteria, known as floc-forming bacteria. To provide adequate oxygen and achieve good contact between the sludge flocs and the water, large amounts of air (oxygen) are pumped continuously into the bottom of the activated sludge basin. Alternatively the water can be oxygenated using **surface aerators**. In this case the water is sprayed into the air as a fine mist so that it takes up oxygen from the air.

In order to break down the organic matter quickly the microorganisms are concentrated in the activated sludge basin. This is achieved by recycling most of the sludge that is removed from the subsequent sedimentation stage. Only a small proportion of the sedimented sludge is removed from the process as excess sludge in order to compensate for the continuous **growth in biomass** (figure 3:6).

Inspection of aerators in an empty activated sludge basin.

Active sludge process



➤ **Figure 3:6** Activated sludge process.

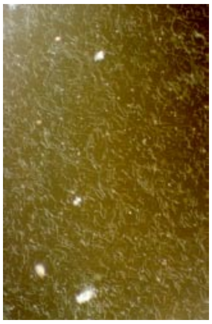
The microorganisms in the activated sludge are able to take up the dissolved organic contaminants in the water and adsorb suspended colloidal particles. This process results in the formation of carbon dioxide, water and biomass.

The organic substances in the water, expressed as BOD, are distributed as follows:

30–50%	are converted to mineral form by oxidising to form carbon dioxide and water
40–45%	are removed from the process as excess sludge
approx. 10%	are removed with the effluent water

The above figures vary with the age of the sludge.

Bacteria in an activated sludge can be divided into three groups: free-swimming, floc-forming and filamentous.


Free-swimming bacteria.

Free-swimming bacteria are single or pair-forming bacteria that are suspended freely in the water. These can be likened to very small particles. The bacteria are so small that they do not have time to fall out as sediment in the following sedimentation stage. The free-swimming bacteria are the ones that multiply fastest in an activated sludge process. But because they are too small to form sediment with the sludge they are flushed out of the activated sludge stage and are lost from the treatment plant. Free-swimming bacteria also serve as food for many of the other microorganisms that are present in the activated sludge process.

There are always free-swimming bacteria in an activated sludge process since they are present in the wastewater that comes into the treatment plant. If they are not eaten up or separated in some other way in the treatment plant then the effluent water will be opaque (cloudy). Low sludge age (see page 52) favours free-swimming bacteria.


Floc-forming bacteria.

The **floc-forming** bacteria normally account for the majority of biomass in an activated sludge process. Floc-forming bacteria are able to grow in clumps because they have a sticky polymer-like surface that makes them stick to each other. As a result they form larger particles (bioflocs) that are large enough to fall out in the subsequent sedimentation stage.


Filamentous bacteria.

The floc-forming bacteria multiply more slowly than the free-swimming bacteria, and therefore require a longer retention time (sludge age) in the activated sludge stage to prevent them being flushed out. The minimum sludge age is 1–2 days. The growth of the bacteria is temperature-dependent, which means that a low water temperature requires longer sludge retention time.

Filament-forming bacteria are bacteria that grow "in-line" and form long, hair-like filaments in the bio-sludge. These bacteria normally multiply the slowest and are favoured by high sludge age, low temperature or unusual conditions in the activated sludge process.

A high concentration of filamentous bacteria can cause severe operating problems in an activated sludge plant. The reason is that they make the sludge so fluffy and bulky that it does not easily fall out in the subsequent sedimentation basin, which can become completely filled with bio-sludge. This means that biological sludge is discharged with the water from the treatment plant and causes elevated emission levels. The bulky sludge also makes it difficult to remove excess sludge and sludge for recycling.

A healthy bio-floc should nevertheless contain a small number of filaments as they give stability to the floc, just like a skeleton. The filament concentration must be low however, as a surplus can cause severe operating problems.

Operating parameters

The most important operating parameters for the activated sludge process are **sludge load**, **sludge age**, **oxygen concentration** and **suspended solids** (SS).

The sludge load is the ratio between the amount of nutrients supplied (= amount of organic matter) and the existing amount of microorganisms.

The sludge load is the ratio of the amount of BOD added each day and the existing amount of sludge (suspended solids) in the aeration basin.

$$F = \frac{Q \times BOD_7}{V \times SS}$$

F = sludge load, kg BOD_7/kg SS, per day

Q = flow rate, m^3/day

V = capacity of aeration basin, m^3

BOD = BOD content of influent water, kg BOD/m^3

SS = sludge content of aeration basin, kg SS/m^3

Treatment processes in activated sludge plants can be classified into three main groups depending on the sludge load (F): **high**, **normal** or **low** load.

The following guide values apply to each group:

High load	**0,8–1,5**	**kg BOD_7 /kg SS per day**
Normal load	**0,3–0,7**	**- ” -**
Low load	**0,05–0,2**	**- ” -**

The average retention time in an activated sludge basin depends on the load on the activated sludge process. A plant with a low load has a large volume and hence a relatively long retention time, while one with a high load can get by with a small volume and hence a short retention time. If the treatment plant has a very effective primary treatment stage (e.g. precipitation) then the volumes can be reduced drastically, since the majority of organic substances are removed at this stage.

➤ **Table 3:6** Retention times for active sludge process.

Process load	Retention time (hours)
High	0,6–2,0
Normal	2,5–6,0
Low	8–24
Long-term aerator	> 24

Sludge age is the average time in days that a sludge particle spends in the aeration basin.

Sludge age is the ratio between the existing amount of sludge in the biological treatment stage and the amount of sludge removed each day.

$$\mathrm{SRT} = \frac{V \times SS_m}{Q_ö \times SS_ö + Q \times SS_u}$$

SRT = sludge age, days (Solid Retention Time)
V = capacity of aeration basin volume, m^3
Q = effluent water flow rate m^3/d
$Q_ö$ = excess sludge flow rate, m^3/d
SS_m = average sludge content of aeration basin, kg SS/m^3
$SS_ö$ = sludge content of excess sludge, kg SS/m^3
SS_u = suspended content of effluent water, kg SS/m^3

Sludge age in plant with	heavy load	1,5–3 days
	normal load	3–8 days
	low load	10–30 days

Oxygen concentration. In an aerobic process oxygen is used continuously to break down contaminants. The oxygen concentration in the process should not drop below 1–2 g O_2/m^3 in order to avoid operating problems. The oxygen consumption depends on the actual sludge load.

The lower the sludge load, the more oxygen is required to reduce a given BOD concentration. If the sludge load is low, oxygen is also needed break down the activated sludge to a greater extent. Low sludge load also leads to nitrification, which considerably increases oxygen consumption.

Oxygen consumption without nitrification is calculated using the formula:

$$S = 0{,}5 \times BOD_{red} + 0{,}1 \times SS_m$$

S = oxygen consumption, kg $O_2/m^3/d$
BOD_{red} = reduced BOD concentration, kg $BOD_7/m^3/d$
SS_m = average sludge concentration in aeration basin, kg SS/m^3

In the case of a normally loaded activated sludge plant, the energy consumption is around 0,9–1,3 kWh/kg BOD_{red}.

Suspended solids

MLSS (Mixed Liquid Suspended Solids)

MLSS is the concentration of suspended solids in the activated sludge basin. The MLSS concentration is normally kept constant in the aeration basin but varies from season to season. Treatment plants with a high sludge age and nitrogen treatment normally have a higher MLSS concentration. The values are in the range 1,5–5 g/l.

MLSS is also a measure of how active an activated sludge plant is. The higher the concentration, the more bacteria there are in the basin. However, MLSS is a measure of suspended solids in the basin, and includes both organic and inorganic SS, so it does not correlate directly with the bacteria content.

VSS (Volatile Suspended Solids)

Many treatment plants also analyse for volatile suspended solids, VSS, which is a measure of the organic content of the activated sludge, and in most cases can be equated with the bacteria content. An example that clarifies the difference between MLSS and VSS is the case of a treatment plant that switched from simultaneous precipitation to pre-precipitation. The VSS content then increased from 67% to 78% because the precipitation chemical contributed to sludge production during simultaneous precipitation. If the SS content was kept constant it led to a 16% increase in the biomass, and hence the same increase in the treatment capacity.

Sludge index

One measure of the sedimentation performance of a sludge is the sludge index, which is obtained by dividing the sludge volume by the concentration of suspended solids in the activated sludge. The sludge volume is the amount of sludge that is obtained after 30 minutes of sedimentation, and is expressed in ml/l. The lower the sludge index, the better the sedimentation performance. Normally the sludge volume index is 60–150 ml/g.

For sludge volumes lower than 300 ml/l the sludge index is calculated using the formula:

$$\text{Sludge index} = 1000 \times \frac{SV}{SS} \text{ ml/g}$$

SV = sludge volume, ml/l
SS = suspended solids, mg/l

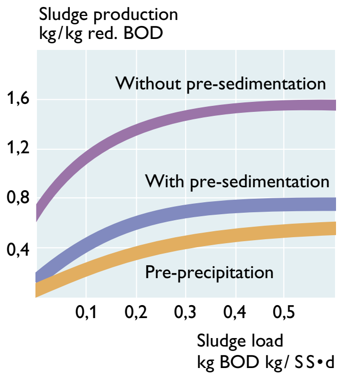
For sludge volumes in the range 300–800 ml/l the following formula is used:

$$\text{Sludge index} = 1000 \times \frac{200 + SV/3}{SS} \text{ ml/g}$$

A high sludge index indicates that something has gone wrong in the activated sludge process. Sludge bulking has occurred, probably as a result of too high concentration of filamentous bacteria, which make water treatment more difficult.

Sludge production

The amount of excess sludge that is produced during the activated sludge process depends on the load on the treatment stage. A normally loaded plant that has a pre-sedimentation stage produces roughly 0,7–0,8 kg of excess sludge per kg of reduced BOD_7. One requirement is that the concentration of suspended solids in the effluent water from the sedimentation stage stays between 10 and 20 mg/l.



➤ **Figure 3:7** Surplus sludge production (kg/kg reduced BOD) against sludge load for three treatment processes.

Energy consumption

An activated sludge process requires large amounts of energy. As mentioned previously, it requires between 0,9 and 1,3 kWh to remove each kilogram of BOD. This energy is not just used for pumping oxygen into the basins. Even if the oxygen concentration is satisfactory, a certain minimum amount of air must be injected to keep the sludge moving. Otherwise, some of the sludge would fall out in the activated sludge basin and the treatment efficiency would be impaired. Normally this is not a problem, since the amount of oxygenating air that needs to be added is greater than the amount of air needed for agitation. If the oxygen requirement is low then the activated sludge basin can instead be equipped with agitators to prevent accidental sedimentation.

The energy consumption of the activated sludge process has fallen in recent years thanks to new types of aerators that permit more efficient oxygenation. Surface agitators are another way of reducing energy consumption since they are normally more energy efficient than bottom injection. Reducing the BOD load on an activated sludge naturally also decreases the energy consumption, since it reduces the oxygen consumption and sludge volumes. The BOD load in the biological stage can be reduced by precipitation, for example.

Treatment efficiency

The degree of reduction of BOD depends on the way the activated sludge process is operated. The more time the bacteria are given to break down the contaminants, the more effective the treatment.

➤ **Table 3:7** Degree of decomposition of BOD in activated sludge process.

Plant with high load	**60–90%**
Normal load	**85–95%**
Low load	**90–99%**

The degree of decomposition also depends on what is in the water. If the influent water contains a high proportion of compounds that are difficult to break down then a longer retention time is required.

Membrane bioreactor

In recent years membrane technology has begun to make an appearance in biological treatment in the form of membrane bioreactors (MBR). These use membranes to separate the bioflocs in an activated sludge process, instead of sedimentation. The membranes have pores that allow the passage of dissolved substances, but not particles.

Biofilm processes

Biological beds

The treatment of wastewater in biological beds is based on a system of sprinklers that allow water to percolate through a bed of material that is also aerated by large quantities of air. The bed supports a culture of microorganisms that live on the organic contaminants present in the water. A large proportion of the organic substances can be removed in this way.

Assuming that there is unlimited access to oxygen, the efficiency of the process depends on the area of contact between the carrier material and the wastewater.

The most common bed material in older plants is crushed stone or pumice with a particle size of 70–90 mm and a specific area of 40–60 m^2/m^3. However, more modern plants use a plastic filler that can have a specific area of 100–250 m^2/m^3. There is less risk of clogging with these new materials, since they have larger cavities.

Sludge separation

When the growth of microorganisms on the carrier material reaches a certain thickness the water trickling through the bed carries away some of the biofilm. This is separated in the form of sludge in the subsequent sedimentation basin.

It should be noted that biological beds usually allow passage of a fraction of finely suspended material that may be difficult to remove. It is therefore recommended that chemical precipitation is carried out after the biobed.

Energy consumption

Biobeds were originally an energy-efficient alternative to activated sludge treatment. But the development of new agitators in recent years means that the difference is now relatively small. In general, the energy consumption is around 0,9 kWh per kg of reduced BOD_7.

Load

A stone-filled biobed can treat 0,8–1,2 kg BOD_7/m^3 of bed volume each day if a BOD reduction efficiency of 80–85% is required. The BOD load can be doubled if biobeds containing plastic filler material are used.

Biobeds with plastic filler are useful for treatment prior to an activated sludge process if wastewater is heavily contaminated and they can be designed to cope with 3–5 kg $BOD_7/m^3/d$. On the whole a biobed is more effective per unit volume than an activated sludge basin.

Treatment efficiency

Biobeds are normally designed for a maximum BOD reduction of 80–85%, and are known as heavily loaded biobeds. Further improvements in treatment efficiency require extensive recirculation of wastewater. For economic reasons it is often cheaper to use the activated sludge process instead. It is however possible to use biobeds for nitrification.

Bio-rotor

The bio-rotor is based on the same principle as the biobed, i.e. the wastewater passes through a carrier material, which in this case is attached to a rotating drum or disc on which the microorganisms grow.

Wastewater passes through a trough in which the bio-rotor is partially immersed. Oxygenation is achieved by rotating the drum.

The sludge production and treatment efficiency are comparable with those of the biobed.

Energy consumption

The process is relatively energy efficient and is often used for small municipal plants and heavily contaminated industrial wastewater. The load on a bio-rotor can be up to 15–30 g BOD_7 per m^2 of rotor area per day. The energy consumption of a bio-rotor is usually given as around 1,1 kWh/kg of reduced BOD_7.

Suspended biofilm (moving bed process)

One technology that is used increasingly often is biofilm processes that have a suspended carrier. The biofilm grows on small plastic floats that float in the water. A sieve in the outflow of the bioreactor prevents the pieces of plastic from escaping with the water. The biofilm that grows on the plastic carrier material eventually works loose and has to be separated after the reactor in the same way as the sludge from a biobed or bio-rotor.

The original process uses a carrier material of polythene with a density of 0,95 g/cm^3. The carrier material is formed from small pieces of tube that are 10 mm in diameter and 7 mm long. The pieces have a cross on the inside and fins on the outside to maximise their specific area. The effective specific area when the tank is two-thirds filled with carrier material (the usual filling density) is 325 m^2/m^3. The high specific area means that moving bed bioreactors are very small and compact. The retention time in a plant designed solely for BOD reduction is 30–60 minutes. A reactor designed for nitrogen reduction has a retention time of 3–4 hours, compared with 12–18 hours for an activated sludge plant that delivers the same efficiency.

The use of suspended carrier material is particularly suitable when the time comes to upgrade an activated sludge plant that already has a large capacity. It is then simply a matter of using as much carrier material as required to achieve the desired treatment efficiency.

This process is also especially suitable for use in combination with chemical post-precipitation in heavily loaded plants, since it permits a very compact plant. There is a major need for plants of this type in many cities that are close to the sea and have limited space available for a wastewater treatment plant.

Biological filters

In recent years, new biofilm reactors have been developed, particularly in France, that are similar to traditional sand filters. In other words the water passes – upwards or downwards – through a filter bed consisting of a coarse filter material that is usually similar to Leca (a lightweight aggregate). The biofilm grows on the surface of the particles.

Incoming sludge and sludge produced by the treatment process itself mean that the filter gradually becomes clogged and must be back-flushed every so often. The plant therefore operates on a discontinuous basis, just like a conventional sand filter. Biological filters are very effective, but are used primarily with pre-treated water and for nitrification, for example.

Fluidised bed

Another way of building compact biological treatment plants is to use fluidised bed technology. Sand grains of a specific size are used as the carrier material for the microorganisms. Wastewater is pumped up through the bottom of a tank at a constant flow rate, which keeps the sand grains suspended in the aqueous phase. This ensures extremely good contact between the microorganisms and the water, which means that the retention time can be kept short.

The disadvantage of this process is that it is difficult to operate under aerobic conditions. It is nevertheless ideal for anoxic operation and can be used for denitrification.

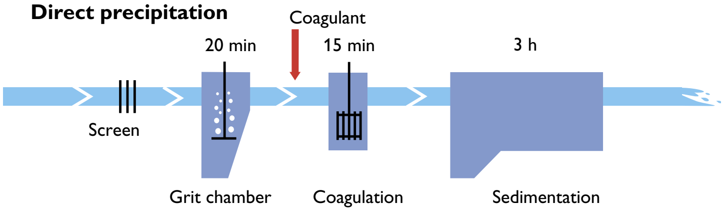
If the respiration process is based on nitrate then a very high bioactivity can be achieved per unit volume. Oxygen cannot dissolve fast enough in the water.

Chemical treatment

Chemical treatment of wastewater can be used in several different treatment systems. Generally, the chemical treatment process consists of a mixing stage, in which the coagulant is mixed with the water. Then comes the coagulation stage, during which suspended flocs develop. These can then be separated in the separation stage by sedimentation, flotation or filtration.

Direct precipitation

In direct precipitation the precipitation stage is the only treatment stage used after the screens and sand trap. In some cases the precipitation stage may be preceded by a pre-sedimentation basin.¨



➤ **Figure 3:8** Direct precipitation. In many cases separate mixing and coagulation chambers are not used.

Reduction during direct precipitation

SS	>	90%
BOD	≈	75%
P_{tot}	>	90%
N_{tot}	≈	25%

The total hydraulic retention time, i.e. the time the water spends in the treatment process, is 3–4 hours.

The precipitation chemicals that are used are aluminium salts, preferably Kemwater AVR or PAX, or trivalent iron salts, such as PIX, or lime. Bivalent iron salts cannot be used.

Direct precipitation is used in many wastewater treatment plants in the Nordic countries and has also gained acceptance as the most cost-effective method in a number of large cities around the world. The process gives a phosphorus reduction of over 90% and a reduction in organic content of around 75%.

➤ **Table 3:8** Treatment efficiency, Norwegian direct precipitation plant.

Parameter	Number of plants	Inlet	Outlet mg/l	Removal efficiency %
BOD_7	23	167 ± 95	27,2 ± 12,7	80,9 ± 9,6
COD	87	463 ± 251	104 ± 38	74,9 ± 7,9
P_{tot}	87	5,24 ± 2,53	0,26 ± 0,16	94,0 ± 5,5
SS	78	233 ± 186	16,6 ± 9,6	90,6 ± 7,9

Ødegaard H. and Karlsson I., Chemical Wastewater Treatment – Value for Money, I: Chemical Water and Wastewater Treatment IV, H.H. Hahn et al (Eds), Springer Berlin Heidelberg New York, pages 191–209, 1994.

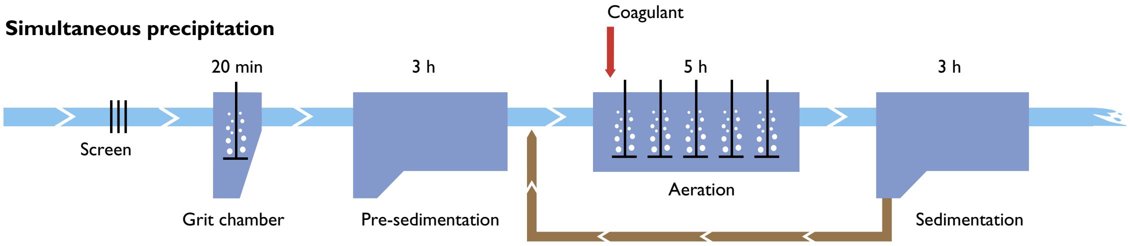
The biological stage also serves as a coagulation basin, and both the biological sludge and the chemical sludge are removed in the subsequent stage.

Direct precipitation can give phosphorus concentrations below 0,3 mg P/l in the effluent water. Existing mechanical treatment plants can be converted to effective direct precipitation plants for a very modest investment.

Simultaneous precipitation

Simultaneous precipitation is the name given to a phosphorus reduction process in which chemical phosphorus precipitation takes place at the same time as biological treatment in an activated sludge process. The biological stage also serves as a coagulation basin, and both the biological sludge and the chemical sludge are removed in the subsequent stage.

The total hydraulic retention time in our example is around 11,5 hours, including pre-sedimentation.



➤ **Figure 3:9** Simultaneous precipitation.

Reduction during simultaneous precipitation

SS	≈	90%
BOD	≈	90%
P_{tot}	>	90%
N_{tot}	≈	25%

This process normally gives phosphorus contents of <1 mg/l in the effluent water.

The coagulant is normally added to either the activated sludge stage or its intake or discharge. Because phosphorus precipitation takes place at the same time as the biological stage it increases sludge production, which considerably reduces sludge age (see MLSS/VSS). This reduces the opportunities for nitrification.

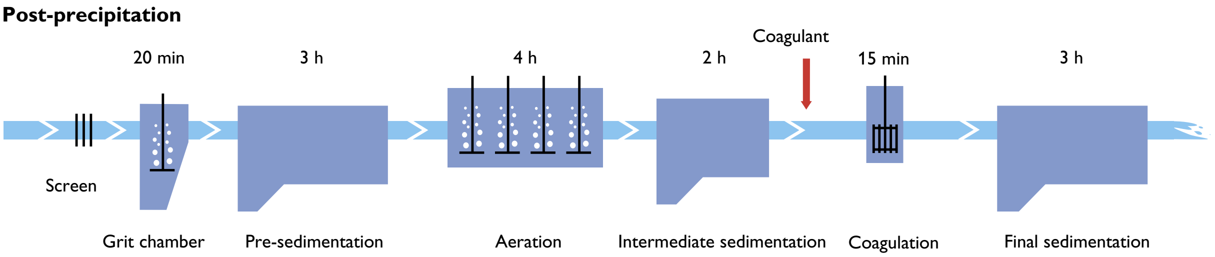
An example can illustrate the change in sludge age as a result of simultaneous precipitation:

A normally loaded treatment plant with a pre-sedimentation stage produces 40 g of biological sludge per person equivalent per day. It is also dosed with 7 g of iron per person equivalent per day, which produces approximately a further 20 g of sludge. The sludge age is thus reduced by 33% if the sludge content is kept constant.

The coagulants that are normally used for simultaneous precipitation are aluminium salts or iron salts (bivalent and trivalent), but not lime. Kemwater PAX (polyaluminium salts) can also be used for simultaneous precipitation and this can also improve the properties of the sludge (see section on Controlling sludge bulking).

Post-precipitation

Post-precipitation is a method suitable for very effective phosphorus reduction. Phosphorus is removed from biologically treated water in a subsequent separate treatment stage.



➤ **Figure 3:10** Post-precipitation.

Reduction during post-precipitation

SS	>	90%
BOD	>	90%
P_{tot}	>	95%
N_{tot}	≈	25%

Post-precipitation gives phosphorus contents of less than 0,5 mg/l in the effluent water.

The total hydraulic retention time in our example is around 12 hours, including pre-sedimentation.

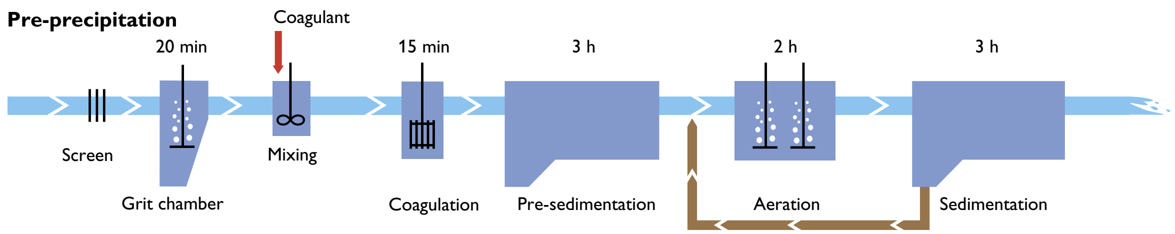
Post-precipitation is often combined with the recycling of chemical sludge to the pre-sedimentation stage. This results in a sludge that thickens more easily, and helps improve the removal of phosphorus and organic material from the pre-sedimentation basin.

During post-precipitation the chemical stage gives valuable additional security if the hydraulic loading is high, since it reduces sludge loss from the biological stage. The biological stage can therefore be made more compact while maintaining or even improving BOD reduction.

The precipitation chemicals used are aluminium salts (PAX and AVR), iron salts (PIX) or lime. Bivalent iron salts cannot be used.

Pre-precipitation

Pre-precipitation is direct precipitation that is followed by a biological treatment stage.



➤ **Figure 3:11** Pre-precipitation. In the vast majority of cases mixing and coagulation chambers are not used.

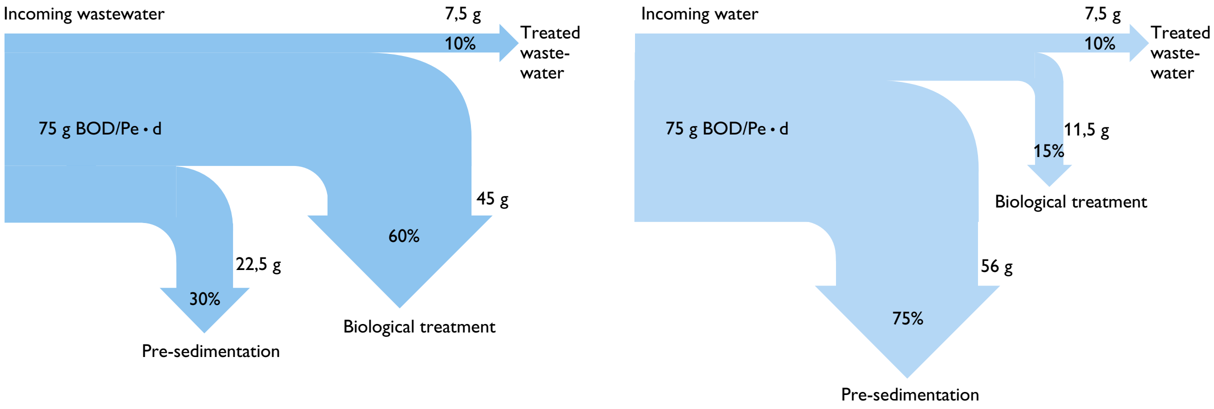
Reduction during pre-precipitation

SS	>	90%
BOD	>	90%
P_{tot}	>	90%
N_{tot}	≈	25%

The total hydraulic retention time is around 9 hours.

Pre-precipitation has been introduced in many treatment plants to reduce the load on the biological stage. No conversion work is usually required, and the coagulant is added at a point where turbulence is high enough to ensure effective mixing before pre-sedimentation.

The pre-sedimentation stage gives a large reduction in organic matter as well as phosphorus. This leads to lower energy consumption and less sludge production in the subsequent biological treatment stage. It also means that the hydraulic retention time can be greatly reduced.



➤ **Figure 3:12** Distribution of organic matter with and without pre-precipitation.

Conventional biological treatment removes around 90% of influent organic contaminants. Around 30% of these contaminants are removed during pre-sedimentation. 10% escape with the effluent water, and the remaining 60% are removed in the biological stage. An activated sludge stage requires around 1,3 kWh per kg BOD. The energy consumption is therefore around 20 kWh per person per year.

During pre-precipitation the distribution of organic material is different. For the same overall treatment efficiency (90%) as in the example above, the distribution might be 75% during pre-sedimentation, leaving just 15% to be removed in the biological stage. This stage can therefore be made much more compact. The energy consumption per person is then just 5 kWh per year, which represents an energy saving of around 75%.

Pre-precipitation also increases the amount of digester gas produced during anaerobic sludge stabilisation. During conventional biological treatment a large proportion of the particulate organic material is converted to carbon dioxide. But during pre-precipitation the particulate organic material remains intact in the sludge, which means that it can be converted to methane gas during the digestion process. This means that considerably more methane gas is generated when pre-precipitated sludge is digested than is the case with biological sludge.

Sludge production from the plant also changes with pre-precipitation. Tables 3:9 and 3:10 show that there is a reduction in the amount of surplus biological sludge (secondary sludge). In comparison with post-precipitation there is no increase in the amount of pure chemical sludge (tertiary sludge).

Sludge production from pre-sedimentation increases with pre-precipitation. This is partly due to the formation of chemical sludge, and partly because more organic material ends up in the sludge during pre-precipitation than during sedimentation alone. The organic material is also removed as primary sludge and is therefore not broken down in the biological stage. After anaerobic or aerobic stabilisation, however, the total sludge content is roughly the same as for conventional treatment.

In volume terms, the quantities of sludge that require dewatering are lower with pre-precipitation than is the case with post-precipitation. There is also a reduction in the amount of secondary sludge, which is difficult to dewater, and this is replaced by primary sludge.

➤ **Table 3:9** Sludge distribution and concentration during **post-precipitation** (before sludge stabilisation).

Post-precipitation	g/pe/d	% TS after thickening	Volume l/pe
Primary sludge	50	6	0,8
Secondary sludge	30	2	1,5
Tertiary sludge	25	2	1,2
Mixed sludge	105	3	3,5

In the case of simultaneous precipitation, the same amounts of sludge are obtained as in post-precipitation, since the chemical sludge is removed with the secondary sludge.

➤ **Table 3:10** Sludge distribution and concentration during **pre-precipitation** (before sludge stabilisation).

Pre-precipitation	g/pe/d	% TS after thickening	Volume l/pe
Primary sludge	110	5	2,2
Secondary sludge	10	2	0,5
Mixed sludge	120	4	2,7

Pre-precipitation spreads out the load on the treatment plant and provides protection against toxic contaminants that could interfere with the sensitive biological stage that follows.

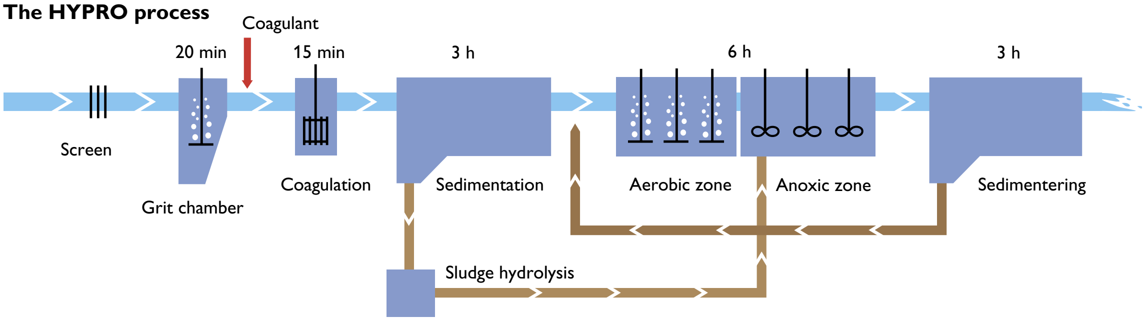
This process is also attractive with regard to energy consumption – especially where energy prices are high. In such cases the cost of precipitation chemicals can be covered by the energy savings alone. In effect this means that phosphorus reduction is "free of charge". The chemical consumption per person per year for pre-precipitation can be estimated at 10–15 kg. This should be compared with an energy saving of 15 kWh per person equivalent per year and a 30% increase in digester gas production.

Suitable precipitation chemicals include Kemwater PIX, AVR and PAX. Lime and iron sulphate cannot be used. Kemwater PAX is especially suitable as a coagulant if the alkalinity of the water is low, as is often the case in northern Scandinavia. PAX reduces the pH considerably more than conventional trivalent precipitation salts. Clearly, the higher the basicity, i.e. OH/Al ratio, of a PAX product, the lower the pH reduction when the product is added to water. This is especially important when operating a plant with nitrification.

Pre-precipitation with nitrogen reduction – the HYPRO process

The HYPRO process is a refinement of the pre-precipitation process that also provides effective nitrogen reduction.

The HYPRO process



➤ **Figure 3:13** The HYPRO process.

Reduction during the HYPRO process

SS	>	90%
BOD	>	90%
P_{tot}	≈	95%
N_{tot}	≈	75%

The total hydraulic retention time, including pre-sedimentation is around 12 hours.

This method is based on using the organic matter in the wastewater as effectively as possible as a carbon source for further nitrogen reduction. In simple terms the process can be divided into two stages. Firstly, organic matter is “borrowed” by pre-precipitation from the wastewater to promote nitrification. Hydrolysis of the organic matter converts it into a more readily accessible form, and it is then returned to promote denitrification.

In addition to phosphorus reduction, the coagulant is also used to separate organic material. The reduction in organic material, often around 75%, changes the BOD/N ratio. The nitrifying bacteria thus have less competition. Sludge production decreases and the nitrifying organisms are able to grow and multiply, which means that the degree of nitrification can also increase.

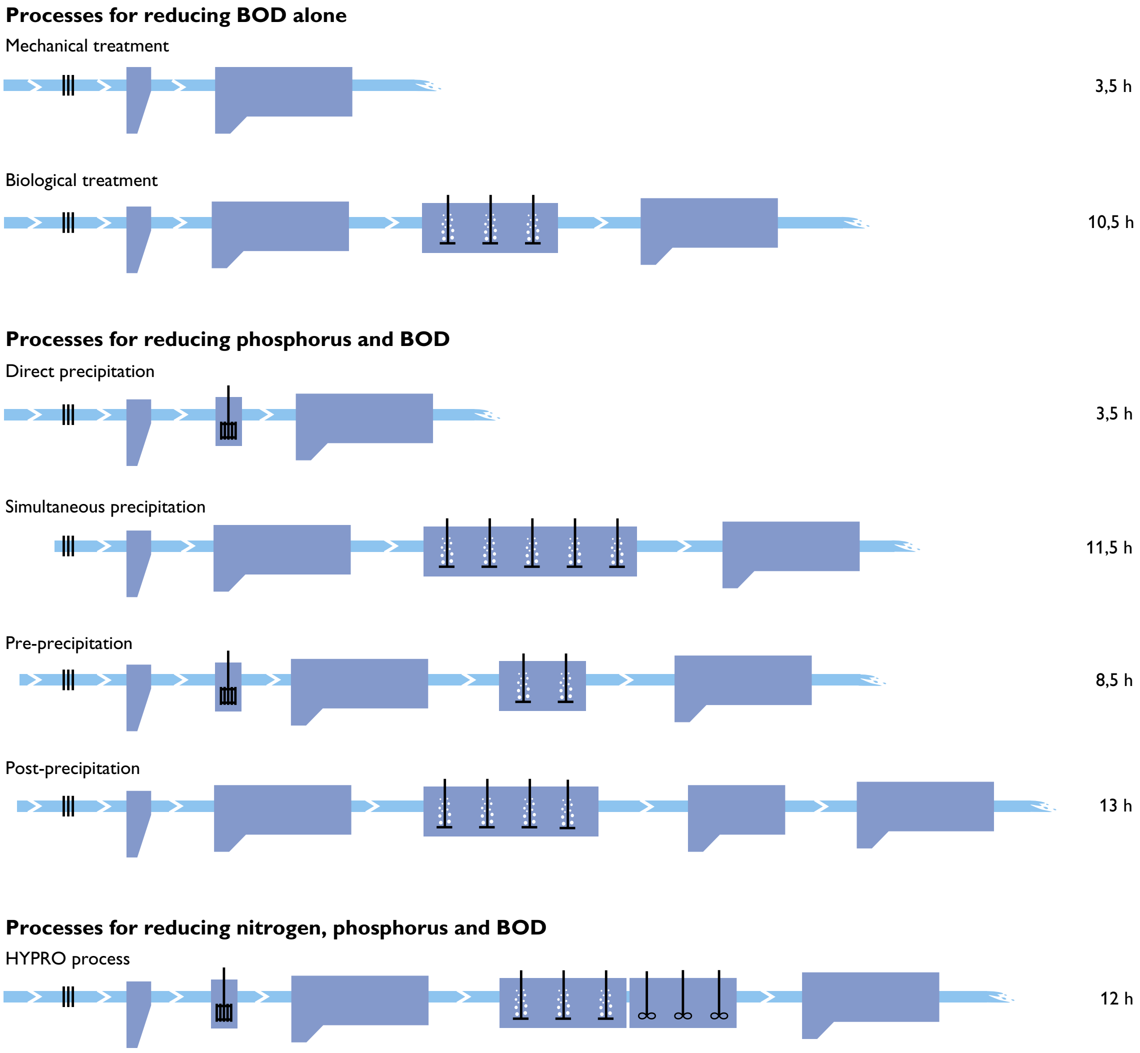
See also the section on Nutrient salt reduction.

Treatment methods

Table 3:11 shows the various processes, treatment results and suitable precipitation chemicals. Detailed descriptions of these processes can be found in the chapter Chemical treatment processes.

➤ **Table 3:11** Comparison between different treatment methods and precipitation chemicals (see also table 3:12).

Method	Treatment efficiency, %		Suitable chemicals		Total treatment time, h
	BOD	P			
Direct precipitation	70–80	>90	AVR PIX	PAX Lime	≈ 3,5
Pre-precipitation	90	>90	AVR PIX	PAX	≈ 8,5
Simultaneous precipitation	90	75–90	AVR PIX	Iron(II)sulphate PAX	≈11,5
Post-precipitation	90	>95	AVR PIX	PAX Lime	≈13



➤ **Figure 3:14** Required retention time for various treatment methods.

Nutrient salt reduction

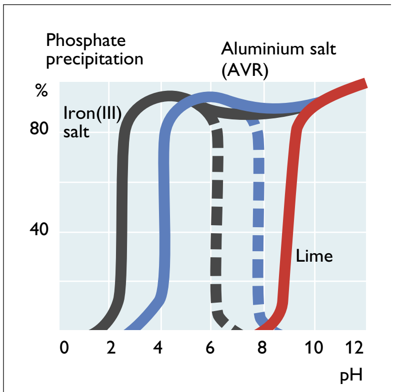
Chemical phosphorus reduction

The chemical precipitation of phosphorus involves using a metal salt to convert the dissolved inorganic phosphorus compounds in wastewater into a low solubility metal phosphate. Organically bound phosphorous is also removed during chemical precipitation since this removes a large proportion of suspended material.

Precipitation chemicals

The chemicals that deliver good treatment efficiency at relatively low cost are:

- aluminium salts
- iron salts
- lime



➤ **Figure 3:15** Orthophosphate precipitation with various coagulants as a function of pH. The dotted lines indicate coagulation in deionised water.

When precipitation chemicals are added they cause the dissolved inorganic phosphates to fall out as insoluble compounds. Because metal hydroxide is precipitated at the same time they form gelatinous flocs that bind together with precipitated metal phosphates and other suspended solids in the water (sweep coagulation). These reactions are pH-dependent, as illustrated in figure 3:15. The particles in the water also coagulate to a greater or lesser extent depending on the type of coagulant used (see chapter 7). Generally speaking, highly charged products such as polyaluminium chloride give more effective coagulation.

Examples of commercial coagulants for wastewater include AVR (ferric aluminium sulphate), PIX (iron salts), PAX (polyaluminium salts) and roast or slaked lime.

Precipitation with aluminium salts

The aluminium ion (Al^{3+}) is the most effective ion for precipitating phosphorus in the form of phosphates from wastewater. The aluminium in coagulants does not just exist in ionic form however. It can also be polymerised to a greater or less degree as polyaluminium ions. The greater the degree of polymerisation the poorer the ability of the product to precipitate phosphates. This is because the aluminium ion has already partially reacted with water and has a lower charge per aluminium atom.

$$Al^{3+} + 2PO_4^{3-} + 3H_2O \rightarrow (AlOH)_3 (PO_4)_2 + 3H^+$$

$$Al^{3+} + PO_4^{3-} \rightarrow AlPO_4$$

$$Al^{3+} + 3H_2O \rightarrow Al(OH)_3 + 3H^+$$

Products in which the active substance is Al^{3+} include Kemwater ALG (granulated aluminium sulphate), AVR (ferric aluminium sulphate) and aluminium chloride. Polyaluminium products include PAX (polyaluminium chloride), PAS (polyaluminium sulphate) and PAN (polyaluminium nitrate). In order to achieve effective precipitation of dissolved phosphorus with aluminium-based products the pH should be kept between 5 and 8,5. It can however be difficult to form flocs at the upper and lower ends of this pH range, depending on the coagulant. Without flocs it is not possible to sediment the precipitated phosphorus, so the pH should preferably be kept between 6 and 8 to ensure effective floc formation. The optimum pH varies from product to product and with water quality.

Theoretically it requires one mole (27 g) of aluminium to precipitate one mole of phosphate (31 g), i.e. 1 g of dissolved phosphorus requires 0,87 g of aluminium. The aluminium does not however react solely with the phosphorus in the water, but also with other compounds, including the water itself, which means that in reality it requires 1–1,5 moles of Al per mole of P, which is equivalent to 0,87–1,3 Al/g of P.

Phosphate precipitation using polyaluminium compounds sometimes requires even higher doses of aluminium. A highly charged polyaluminium product may require more than twice the dosage of aluminium to achieve the same degree of reduction in dissolved phosphorus as an aluminium sulphate. However, polysalts are considerably more effective at depositing suspended solids, i.e. including particle-bound phosphorus. Polyaluminium products are normally active over a wide pH range and produce a lower salt load and have less influence on the alkalinity of the water. The better coagulation characteristics require a lower dosage and hence result in less sludge production than aluminium sulphate.

The total phosphorus content is not normally the deciding factor in how much coagulant should be added to achieve effective phosphorus reduction during pre-precipitation, since part of that phosphorus is bound to particles. It is only when the proportion of dissolved phosphorus is high that the amount of coagulant has to be adapted to the phosphorus concentration. One advantage of using aluminium compounds as precipitating chemicals is that the deposited phosphate remains stable even when the oxygen concentration is low. This means there is no risk of dissolution if the sludge is subsequently digested.

Precipitation with trivalent iron salts

Trivalent iron salts may be based on sulphate or chloride or nitrate. Such products may also consist of a mixture of these salts. Like aluminium precipitation, phosphorus and hydroxide precipitation are governed by the following formulae.

$$3Fe^{3+} + 2PO_4^{3-} + 3H_2O \rightarrow (FeOH)_3(PO_4)_2 + 3H^+$$

$$Fe^{3+} + PO_4^{3-} \rightarrow FePO_4$$

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+$$

Iron(III) salts are effective at precipitating orthophosphates and polyphosphates in the pH range 4–8. As with precipitation using aluminium salts, the combined effect of the calcium ions in the water and the trivalent iron ion results in relatively good precipitation of orthophosphates in the pH range 6–9. Iron and calcium ions do not produce any precipitation in this range individually. The best results and coagulation performance are obtained in the pH range 5–6, where hydroxide precipitation is most effective. Normally, however, there is no problem with precipitation at considerably higher pH values. See also figure 3:15.

The precipitation of orthophosphate requires 1–1,5 moles of Fe^{3+} per mole of P.

Aluminium and iron(III) ions behave identically in this respect.

The precipitation of 1 g of dissolved phosphorus requires 2,7 g or iron or 1,3 g of aluminium.

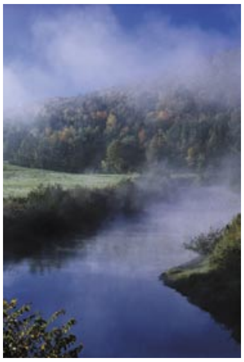
Precipitation with bivalent iron salts

Iron(II) salts are often based on sulphates and are formed as by-products during certain industrial processes.

Bivalent iron cannot be used to coagulate organic matter, only to bind phosphorus.

$$3Fe^{2+} + 2PO_4^{3-} \rightarrow Fe_3(PO_4)_2 + 2H^+$$

Once again, the actual dosage of bivalent iron that is required is usually higher than the theoretical dosage (1,5 mol Fe/mol P). A reasonable dosage of iron to precipitate one gram of phosphorus from phosphate is 3,5 grams.



The liming of Swedish lakes and waterways was increasingly adopted in the 1970s to counter the effects of acid rain. Liming raises the pH of the water and restores its ability to support fish and diverse flora and fauna.

Because of the inability of iron(II)salts to form flocs they are only useful for simultaneous precipitation, during which the iron oxidises as a result of aeration (primarily in the biological stage), and the resulting flocs are separated together with the biological sludge. A long aeration period is required to produce acceptable treatment results.

$$4Fe^{2+} + O_2 + 2H_2O \rightarrow 4Fe^{3+} + 4OH^-$$

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+$$

Each gram of Fe^{2+} that is oxidised requires 0,14 grams of O_2. The oxidation rate of the iron ions is heavily pH-dependent. The oxidation rate can be increased by adding lime to raise the pH.

Precipitation with lime

Calcium ions are effective at precipitating orthophosphate as hydroxyapatite when the pH exceeds 10,5. Lime provides the necessary pH increase for precipitation. Polyphosphates are also precipitated.

$$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3$$

$$10Ca^{2+} + 6PO_4^{3-} + 2OH^- \rightarrow Ca_{10}(PO_4)_6(OH)_2$$

The amount of lime required is not determined by the phosphate content, but primarily by the carbonate content and alkalinity of the water. Carbonate is actually precipitated in the form of calcium carbonate when the pH is raised above 9. Lime precipitation produces a lot of sludge, although this is easily dewatered. When precipitating with lime the pH of the water must normally exceed 11 to produce a precipitate that can be separated readily. At this pH the original alkalinity of the water is also restored. The alkalinity would normally be reduced through precipitation of the carbonates in the water.

Nitrate-based coagulants

The cations in iron and aluminium-based products are normally sulphate or chloride ions. It is possible to partially or totally replace these with other anions, of which nitrate is the most common. A coagulant that contains nitrates can be used in more ways than a chloride or sulphate-based product.

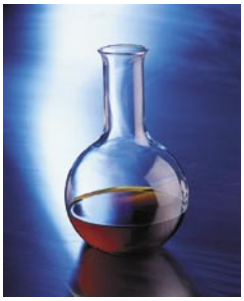
After pure oxygen, nitrate provides the best source of oxygen for bacteria. The nitrate is broken down into nitrogen gas and water, while organic material is broken down simultaneously to form biomass and carbon dioxide (see also the section Denitrification). Most of the organic matter that is broken down is the more readily degradable type that is dissolved in the water. Dissolved organic material is difficult to precipitate, and even then can only be reduced by using an aluminium nitrate or iron nitrate.

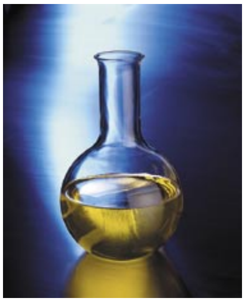
There are several ways of using nitrate-based products. One way is to first precipitate particles and phosphorus from the wastewater in a conventional pre-precipitation plant. The water, which is then free from particles but still contains nitrate and dissolved organic matter, is then passed through a biological stage, often using a submerged biofilter or a basin of carrier material. In the biological stage the organic matter is broken down and the nitrate is converted to nitrogen gas. The extent of removal of organic material can be controlled by adjusting the dosage of nitrate.

There is also the possibility of using the bacteria that always live in sewers. If the coagulant is added to the sewer before it reaches the treatment plant then dissolved organic material can be reduced by respiration with nitrate before the water even reaches the treatment plant. When the wastewater arrives at the treatment plant the particles and phosphorus must then be coagulated, possibly aided by a small amount of polymer to strengthen the flocs, and can then be removed during primary treatment.

The use of nitrate-based products can improve the removal of organic matter in a direct precipitation plant. Alternatively, they can be used to reduce energy consumption in a treatment plant that has a secondary treatment stage.

Nitrate-based products can also be used for other applications. The most common is to neutralise odour (hydrogen sulphide), as described on page 87. These products are also suitable for use where a low salt content is required in the effluent water. This may be useful in warmer areas and along rivers, where the water is used several times before it reaches the sea. Sulphates and chlorides leave the treatment plant with the treated wastewater and thus increase its salt content. Nitrates, on the other hand, are converted and leave the plant as airborne nitrogen.





Dissolved organic matter is difficult to precipitate out, but can be removed by using an aluminium nitrate or iron nitrate.

Comparison between coagulants

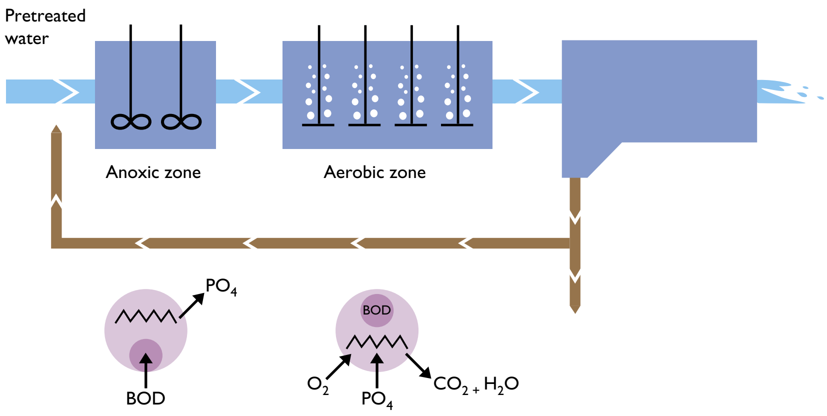
The various coagulants have different physical and chemical properties. They are supplied either in solid form, or as a solution. A comparison of these chemicals is given in table 3:12.

➤ **Table 3:12** Physical and chemical properties of some coagulants.

Coagulant	Composition	Supply form	Density tonnes/m³	Metal content %	mol per kg
AVR	Al and Fe(III) sulphate	granules	1	Al 8,1 Fe 0,7	3,1
PIX	$FeClSO_4$ $FeCl_3$ $Fe_2(SO_4)_3$	liquid	1,4–1,5	Fe 11,5–14	2,0–2,5
PAX	Polymerised Al salts	liquid	1,2–1,4	Al 5–10	1,9–3,7
		powder	0,9	Al 16	5,6
Iron(II) sulphate	$FeSO_4 \cdot 7H_2O$	crystals	1,2	Fe 18	3,2
Lime	$Ca(OH)_2$	fine granules powder	0,6		

Biological phosphorus removal

An alternative to chemical phosphorus removal is the biological method, known as bio-P. This method exploits the ability of certain bacteria to take up unusually large amounts of phosphorus from phosphate. This enhanced phosphorus uptake is achieved by "stressing" these microorganisms, by alternately exposing them to anaerobic and aerobic conditions. The bacteria take up phosphorus in the form of polyphosphates.



➤ **Figure 3:16** Biological phosphorus removal.

Bio-P bacteria have a greater ability to store energy (phosphorus) than other bacteria in a treatment plant. The bacteria can then use this energy when they encounter poorer conditions, such as a lack of oxygen. This is exactly what happens in the bio-P process. During the first stage, which is anaerobic, i.e. free from oxygen and nitrate, recycled sludge is mixed with the wastewater. The wastewater contains a lot of "food" (organic matter) but no oxygen (to generate energy). The bacteria want to make use of this food and store it away. In order to do this they need energy, and this is where the bio-P bacteria have an advantage over other bacteria, since they can store more energy in the form of phosphates. Once this energy has been used, the bacteria release the phosphates. During the anaerobic stage, the concentration of phosphates in the water rises above that of the influent water, while the BOD/COD content falls.

The second, aerobic stage of the bio-P process is the opposite of the anaerobic stage. In this case there is oxygen for energy production but a lack of food (due to competition between organisms). The bio-P bacteria therefore use their stored food to build biomass, while also taking this opportunity to store away polyphosphates for poorer times.

During the aerobic stage the phosphorus content of the wastewater is reduced to a level lower than that of the influent water. The bacteria then fall out in the subsequent sedimentation stage and are pumped back to the anaerobic zone. Some are removed as excess sludge.

Under stable operating conditions the above processes give P_{tot} values of between 0,5 and 2 mg P/l in the effluent water. The relatively high value is partly explained by the fact that the suspended material in the effluent water has a high phosphorus content. Effluent wastewater with a SS content of 20 mg/l can give a phosphorus contribution of 1,2 mg P/l in addition to the contribution that the dissolved phosphorus makes, which is seldom less than 0,7 mg/l.

The difficulty of maintaining a stable process is due to the fact that phosphorus immediately goes into solution if the sludge is exposed to anaerobic conditions in the sedimentation basin or during sludge treatment, such as sludge digestion. Although it is possible to achieve effective phosphorus reduction using the bio-P process, it is usually supplemented by chemical precipitation to ensure good reduction efficiency.

Most bio-P processes are combined with biological nitrogen reduction.

Nitrogen removal

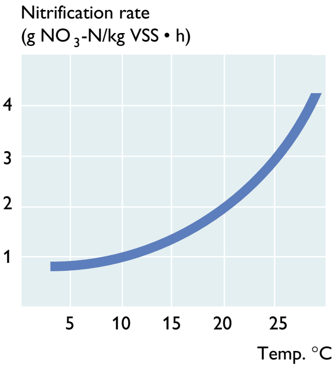
In municipal wastewater treatment plants that operate nitrogen reduction this is almost exclusively done using biological methods. The following is a description of how the various nitrogen treatment processes work and how they can be made more efficient with the aid of chemical precipitation. Alternative methods of nitrogen reduction are also described.

Biological nitrogen treatment

All wastewater treatment plants remove some nitrogen. A small proportion of the total nitrogen content is bound to particles and is separated during the primary treatment. If the treatment plant also uses biological treatment then some of the nitrogen will be taken up by the biological sludge, since nitrogen is a nutrient and an important building block for all life. Around five grams of nitrogen is taken up when 100 grams of BOD is removed during biological treatment. This form of nitrogen reduction is called assimilative nitrogen reduction.

These two nitrogen reduction processes are still not sufficient if extensive nitrogen reduction is required. A more sophisticated nitrogen treatment process must be introduced.

In wastewater the majority of nitrogen is in the form of ammonium (NH_4^+). Ammonium is the cation of ammonia, and as an ion it is difficult to precipitate out (see section on magnesium ammonium phosphate precipitation). Conventional chemical treatment with iron or aluminium salts cannot separate ammonium. Instead, biological methods are generally used to remove the nitrogen in a two-stage process – nitrification followed by denitrification. This type of nitrogen treatment process, in which nitrogen is removed from the water as nitrogen gas, is called dissimilative nitrogen reduction.



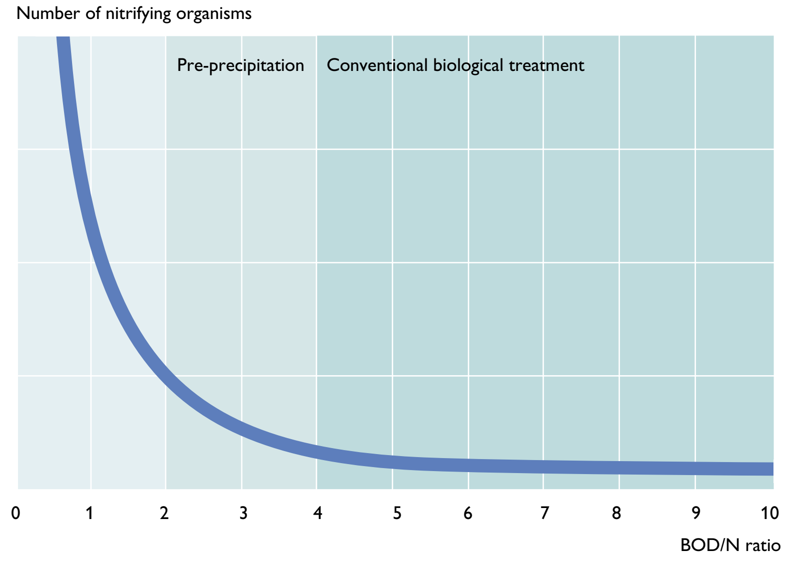
➤ **Figure 3:17** Nitrification rate at different temperatures.

Nitrification

Nitrogen in the form of ammonium must first be converted to nitrate (NO_3^-) before it can be removed from wastewater. This is done using a biological process known as a nitrification process. Autotrophic bacteria use oxygen in the air to oxidise ammonium to nitrate in two stages.

$$\begin{array}{lcl} NH_4^+ + 1{,}5O_2 & \rightarrow & NO_2^- + 2H^+ + H_2O \\ NO_2^- + 0{,}5O_2 & \rightarrow & NO_3^- \\ \hline NH_4^+ + 2O_2 & \rightarrow & NO_3^- + 2H^+ + H_2O \end{array}$$

As can be seen from these formulae, the nitrification process produces acid. This reacts with the carbonate in the water, and if the alkalinity of the water is low (low carbonate content), then the pH may drop sharply during nitrification. This inhibits the nitrifying bacteria, since they work best at a pH between 8 and 9. The nitrite-oxidising bacteria do not take up ammonium, but ammonia, which is in equilibrium with the ammonium in the water. At a higher pH a larger proportion of the nitrogen occurs as ammonia and is more readily taken up by the bacteria. If the pH drops below 5,5 the nitrification process will stop completely. The oxidation of nitrite is however favoured by a lower pH, so the pH must not be too high in the nitrification process.



➤ **Figure 3:18** Effect of BOD content on a nitrifying system.

Temperature also has a major effect on the rate of nitrification. It is possible to carry out nitrification right down to 4°C, but the bacteria work very slowly at this temperature. This means that the sludge age must be kept high, perhaps as much as 20 days, and this would require large basin capacities for biological treatment. Because the BOD-reducing bacteria are more effective than the nitrifying bacteria it is an advantage if the BOD content is low, as this favours fast and effective nitrification.

Nitrification can take place on a fixed carrier material or in suspended cultures. The former process has shown greater tolerance to variations in pH.

Denitrification

Denitrification means that microorganisms reduce nitrite or nitrate to nitrogen gas while oxidising organic matter in the absence of oxygen. The resulting nitrogen gas is ventilated into the atmosphere.

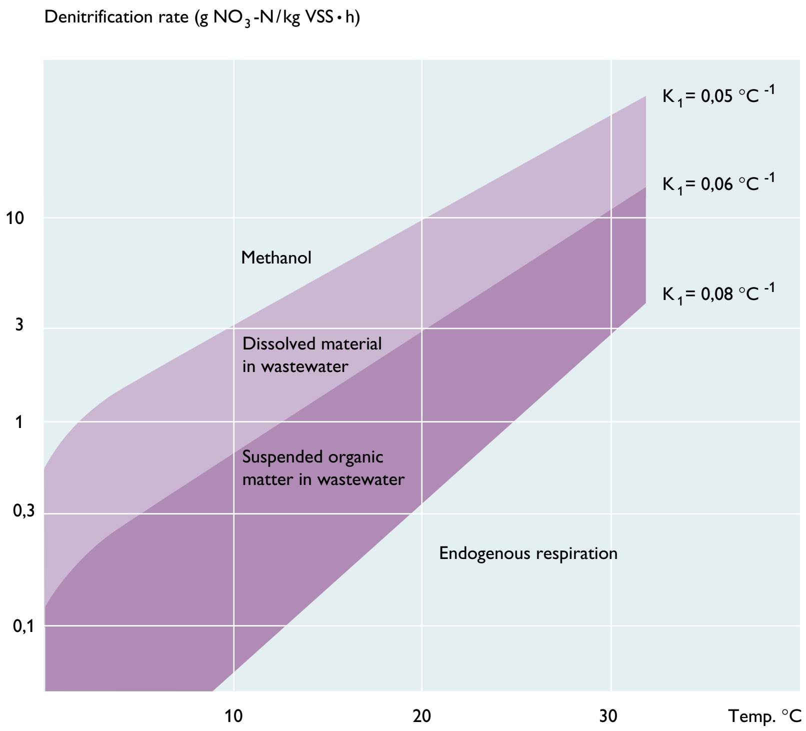
$$2NO_3^- + H^+ + \text{organic matter} \rightarrow N_2 + HCO_3^-$$

The organisms that can use both oxygen and nitrate for this oxidation process are known as facultative anaerobes. They prefer oxygen, as this gives a slightly higher energy yield. Because of this, oxygen must be excluded from the nitrification process. Anoxic conditions must apply, i.e. the water must be free from dissolved oxygen, but it must contain oxygen bound up as nitrate. These organisms are heterotrophic and need organic carbon as a substrate. The optimum pH for the denitrification process is between 7 and 9.

As indicated by the formula, the process leads to an increase in alkalinity. Half of the alkalinity that is lost during the nitrification process is recovered.

The sources of carbon for denitrification can be divided into two groups, internal and external.

When we refer to internal carbon sources we mean that the organic content of the wastewater itself is used for nitrate reduction. This organic material can however cause wide variations in the rate of denitrification. The dissolved fraction gives the highest rate.



➤ **Figure 3:19** Denitrification rate for various carbon sources.

However, this fraction is usually insufficient to achieve more than a 50% reduction in total nitrogen. If the retention time is long then more inaccessible internal carbon sources, such as particulate organic matter in wastewater, can be utilised. Internal carbon sources also include the degradation of biological sludge during the process known as endogenous respiration.

To achieve a considerably higher reduction rate the organic fraction of precipitated sludge can be used as a carbon source, following biological or chemical decomposition by sludge hydrolysis.

External carbon sources are easily biodegradable materials, such as methanol, ethanol, acetic acid or starch, which are added to the process. This is costly, so external carbon sources should only be used to supplement internal sources.

The removal of one gram of nitrogen requires a carbon source equivalent to 3–6 grams of COD. The denitrification rate is temperature-dependent, but not to the same degree as the nitrification rate.

➤ **Table 3:12** Characteristics of some sources of carbon.

Product	Denitrification rate $g\ NO_3^- - N/kg\ VSS{\bullet}h$	COD content $mg\ O_2/l$
Glycol	7–10	1400
Acetic acid	12–16	800
Propylene glycol	16–17	1580
Acetate/methanol	10–15	1110

Denitrification processes

There are several methods for denitrification in a biological treatment process: pre-denitrification, post-denitrification or combinations of these processes. There is also simultaneous or discontinuous denitrification.

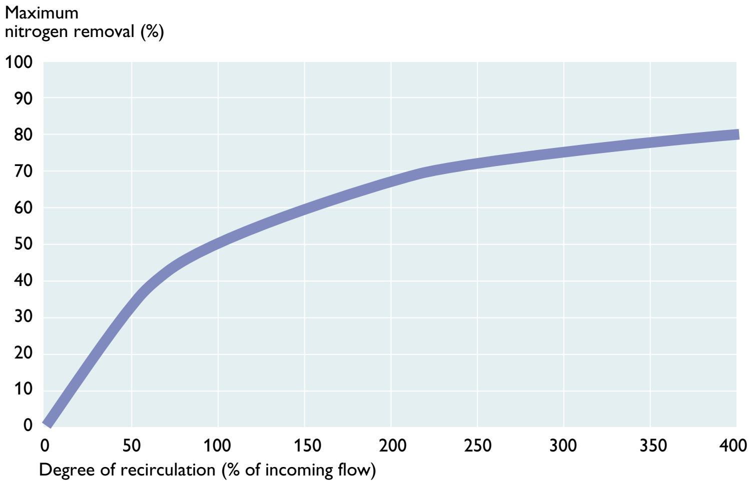
Pre-denitrification

This process uses the organic matter (BOD) in the influent wastewater as a carbon source. The nitrate that is produced in the subsequent aerobic zone is recirculated, either with recycled sludge alone, or with recycled sludge and water from the aerobic zone. The degree of nitrogen reduction depends on the degree of recirculation.

The advantage of this method is that it uses readily available BOD in the wastewater. Chemical pre-treatment does not have to be a drawback if the retention time in the anoxic zone is short, since the readily available dissolved organic matter is still available after precipitation. However, if the retention time in the anoxic zone is long, the source of carbon can be lost through precipitation.

Pre-denitrification and post-denitrification can be usefully combined to obtain optimum benefit from the organic content of the water. When combined with chemical pre-precipitation the precipitated organic matter obtained after sludge hydrolysis can be used as a readily available source of carbon.

Maximum degree of nitrogen breakdown (%)

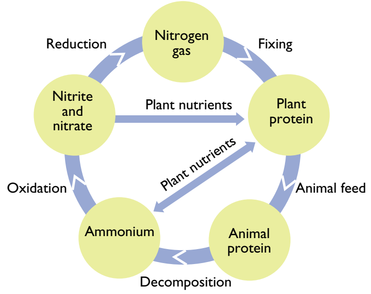


➤ **Figure 3:20** Maximum nitrogen reduction(%) during pre-denitrification against degree of recirculation.

Post-denitrification

All the wastewater goes first through an aerobic zone where both BOD and nitrogen are oxidised. The water that passes into the following anoxic zone is poor in BOD and rich in nitrate and microorganisms. Nitrate reduction can now proceed if organic material (a source of carbon) is added.

The carbon source that is used is readily available organic matter, such as acetates, alcohols, starches or hydrolysed primary sludge. The rate of denitrification and the space required depend largely on the composition of the carbon source.



➤ **Figure 1:3** The nitrogen cycle.
(from chapter 1 page 8)

The advantage of post-denitrification is that a high proportion of nitrogen can be removed without the need for added recirculation. This is however necessary in the case of pre-denitrification, if more than 50% of nitrogen is to be removed.

It is important to get the maximum benefit from the organic matter in the wastewater itself, since external sources of carbon are expensive. For example, if methanol is used it would theoretically take 2,8 grams of methanol to remove one gram of nitrogen. In practice the real figure may be higher.

The HYPRO process is based on pre-precipitation and the hydrolysis of primary sludge. This process reduces the volume required by both the nitrification and denitrification processes. The low BOD/N ratio gives a high nitrification rate. Pre-precipitation "separates" the carbon sources so that only easily accessible carbon remains, which is suitable for pre-denitrification.

The less accessible precipitated organic matter can be hydrolysed in concentrated form, as primary sludge, and returned for denitrification in a more accessible form. This allows the treatment plant to be self-sufficient in carbon.

Suitable coagulants for the HYPRO process are PIX, AVR and PAX. Lime and bivalent iron cannot be used.

Simultaneous denitrification

This process combines both aerobic and anoxic conditions in the same treatment basin. Surface aerators create aerobic conditions immediately adjacent to the aerators. Before the water reaches the next aerator the conditions become anoxic and denitrification can proceed. This process is used in ring canal systems with very long retention times – often up to several days.

Sequenced Batch Reactor (SBR)

Reject water from sludge dewatering can be treated in a separate biological reactor that operates in a sequence – filling, nitrification, denitrification, sedimentation and emptying – then the sequence starts again. Often two reactors are used.

Chemical-physical nitrogen treatment methods

Some chemical-physical methods for removing nitrogen are described below. These methods are normally applied to highly contaminated wastewater with high nitrogen contents. They are therefore used mainly to treat reject water or industrial wastewater. The most common methods are stripping and magnesium ammonium phosphate precipitation.

Breakpoint chlorination

In breakpoint chlorination, ammonium in wastewater is oxidised to produce nitrogen gas, which escapes into the atmosphere. Organically bound nitrogen is not oxidised however. Other disadvantages of breakpoint chlorination are the high operating costs and the risk of producing toxic chlorinated hydrocarbons.

Ion exchange

Wastewater is made to pass through an ion exchange medium in which ammonium ions become attracted to the surface of the medium. The ion exchange medium can be regenerated using kitchen salt. There is a waste problem, since this process produces an elute of concentrated ammonium solution.

This method is disrupted by suspended matter in the water and is also relatively costly where large flow rates are involved. Natural minerals, such as zeolites, can also be used. These are not usually regenerated but can be mixed with the treatment plant sludge.

Ammonia removal

When the pH of wastewater is raised above 11 a large proportion of its ammonium is converted to dissolved ammonia gas. This ammonia can be driven off, or stripped, by injecting air or passing the wastewater through a column. The ammonia should be recovered in an absorption column. This method requires large air flow rates to treat wastewater, around 3 m^3 air/l. There is also a risk of carbonate precipitation, which can cause clogging. This process is however suitable for treating highly contaminated water, such as reject water.

Ammonia can also be driven off at high temperature, by steam stripping.

Membrane technology

Dissolved nitrogen compounds can also be removed from water with the aid of a very fine-pored membrane. This method requires pressure, which entails high energy costs.

MAP precipitation

Magnesium ammonium phosphate (MAP) is a double salt that is also known as struvite. If the water contains the same molar concentrations of phosphorus and ammonium, precipitation can be achieved by adding magnesium and maintaining the pH above 7,5. Struvite precipitation is a familiar method in many wastewater treatment plants, particularly those that use the bio-P process. In digesters and the piping leading from them the ammonium and phosphate contents can be high enough to promote MAP precipitation. This undesirable precipitation causes blockages in pipes. Undesirable MAP precipitation can be prevented by ensuring that an adequate concentration of coagulant is present in the sludge to bind the phosphates.

The nitrogen content of wastewater is usually considerably higher than the phosphate content. This means that phosphates must be added to achieve effective nitrogen reduction. Adding phosphate is costly and may seem illogical, since one of the requirements the treatment plant has to meet is the reduction of phosphorus.

Other chemical methods in wastewater treatment

Controlling sludge bulking

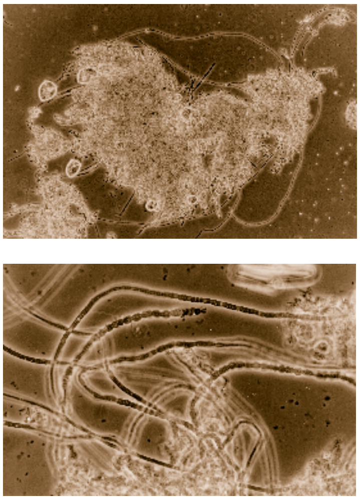
Sludge bulking is a problem that occurs when an activated sludge does not work effectively. The cause of the problem is usually the excessive growth of filamentous bacteria, which produce fluffy flocs. The problem can be solved in a variety of ways, depending on the type of filamentous bacteria that is causing the bulking.

One common method is to adjust the process parameters in the activated sludge basin. This is naturally the normal course of action, but it is not always sufficient to remedy the problem.

There are a number of chemical methods of combating filamentous bacteria. The commonest method in the past was to add an oxidising agent, such as chlorine, hypochlorite or hydrogen peroxide to the water. The oxidising agent then reacts with the projecting filaments, which die. This method is fast and effective, but may be regarded as aggressive. The oxidising agent reacts with everything in its path, which means that micro-fauna can also be killed, impairing treatment efficiency.

A gentler method is to add modified polyaluminium chloride to the activated sludge basin. It has been shown that treatment plants that use polyaluminium chloride rarely have problems with filamentous bacteria. If modified PAX is to be used solely to prevent sludge bulking it is recommended that this product is added at the same time. The dosage of PAX is normally lower than is required for conventional water treatment.

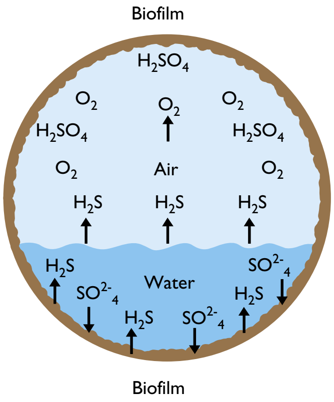
This method has been shown to be extremely effective in a large number of treatment plants that have problems with sludge bulking. The effect is not instantaneous, but maximum effect is achieved after around 2–4 weeks. The advantage of the method is that the activated sludge and micro-fauna are not harmed by PAX. The product is also easier to handle than an oxidising agent, and it improves phosphorus reduction. The drawback of this method is that it takes time to become fully effective against all types of filamentous bacteria. The method has nevertheless been shown to be extremely effective when sludge bulking is caused by the bacteria Microthrix parvicella and Type 021N.



➤ **Figure 3:21** Filamentous bacteria in activated sludge.

Odour neutralisation

Odour, or smell, is something that is often linked to treatment plants and sewers. This odour is often caused by hydrogen sulphide. Hydrogen sulphide is formed by bacteria when water is septic. The bacteria in the water that can break down organic material prefer to use oxygen as an electron acceptor. If oxygen is not present then the next in line is the nitrate ion, followed by the ferric ion (trivalent iron ion) and then the sulphate ion. Because nitrate and ferric ions are rarely present in wastewater it is the sulphate ion that is used as electron acceptor once the oxygen has been used up. The sulphate ion is then converted to hydrogen sulphide (H_2S). This happens mainly in pressurised sewers.



➤ **Figure 3:22** Formation of hydrogen sulphide and sulphuric acid in a sewer pipe.

Hydrogen sulphide is a colourless gas with a distinctive smell of rotten eggs. The gas is highly toxic and has a very strong smell even at low concentrations. Because hydrogen sulphide is heavier than air there is a risk that the concentration of hydrogen sulphide in unfilled spaces in sewers will reach dangerous levels. There have been several cases of workers being killed by hydrogen sulphide gas while working in sewers.

Hydrogen sulphide is not only evil smelling and highly toxic, but it can also be converted to sulfuric acid by certain types of bacteria. This takes place in unfilled spaces in sewers. The bacteria that convert hydrogen sulphide into sulfuric acid live on the inside surface of the pipes and are extremely resistant to acid environments; they can withstand a pH of less than 1. At such low pH the sewer pipes corrode rapidly, and sooner or later the sewer will collapse. This phenomenon is well known and can be extremely costly.

In order to prevent this corrosion the formation of hydrogen sulphide must be prevented, or vulnerable areas of the sewers can be lined with plastic. The only way to eliminate the odour and health risk is to prevent formation of hydrogen sulphide.

One effective method of preventing hydrogen sulphide formation is to ensure that the water is always well oxygenated. This is not always possible in pressurised lines with a long retention time.

In such cases something must be added to the water to prevent hydrogen sulphide from forming. Normally, iron or nitrate is used. The three groups of products described below are used most often to combat hydrogen sulphide formation.

Nitrate

As mentioned above, nitrate is a good acceptor of electrons when oxygen is not available. If nitrate is present in the water it drastically reduces the risk of hydrogen sulphide formation. Adding nitrate to the sewer network is a preventive method. However, it is important to add sufficient nitrate to prevent hydrogen sulphide formation throughout the sewer network, but no more than will be completely used up by the time it reaches the treatment plant, otherwise it simply adds to the nitrogen load. Some method of controlling the dosage is therefore advisable.

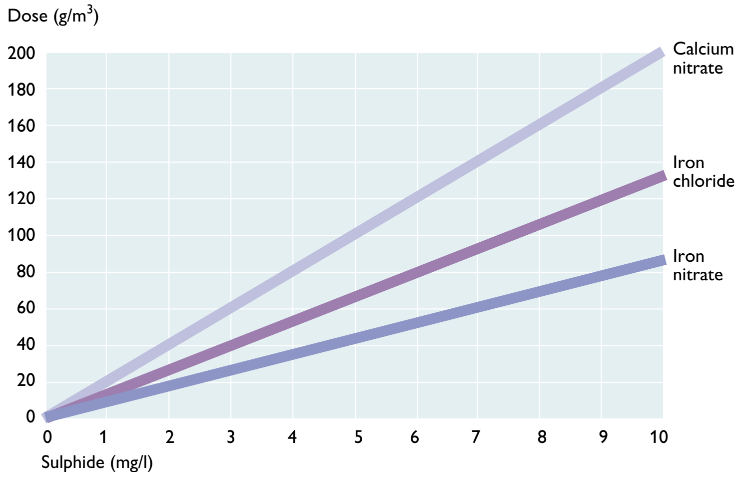
The advantage of using nitrate salts is the preventive effect they have, and the fact that they partially reduce the organic load on the treatment plant. The disadvantage is that they sometimes generate large quantities of nitrogen gas (see page 80), which can cause problems in the transport of wastewater. Uncontrolled dosage can also increase the nitrogen load on the treatment plant.

Nitrate-based products that are used to combat hydrogen sulphide include calcium, sodium and magnesium nitrates.

Iron

When iron ions combine with the sulphide ion, which is the anion in hydrogen sulphide, they form salts with low solubility. This means that if a bivalent or trivalent iron salt is added to wastewater, it will react with the hydrogen sulphide in the water and prevent it from going into the gas phase. This approach differs from the nitrate method in that the hydrogen sulphide is allowed to form before it is removed.

If trivalent iron is added to the water before the hydrogen sulphide has formed it will however have a certain preventive effect, since, as mentioned above, the bacteria prefer trivalent iron (ferric) to sulphate as an electron acceptor.



➤ **Figure 3:23** Dosage of three different products against amount of sulphide removed.

The advantage of using iron is that it is usually a more economical method than using nitrates. It is also less important to control the dosage, as long as it is high enough, since surplus iron is later used for floc formation and phosphorus reduction in the treatment plant. The disadvantage of iron-based products is that they lead to a small increase in sludge production at the treatment plant.

Iron nitrate

Iron nitrate is a combination of the two products mentioned above. Because of this, iron nitrate has a powerful inhibiting effect on hydrogen sulphide formation, as well as a good reduction efficiency even if sulphides do form in the sewers. Iron nitrate is so unique in this respect that it can be regarded as a separate product whose characteristics make it far superior to the other two groups of products.

In contrast to municipal wastewater, the contaminants in industrial wastewater differ widely depending on the type of industry. The advantage of treating water at the industrial plant itself is that the nature of the contaminants in the wastewater is often known and it can be treated accordingly.

Treatment of process water and industrial wastewater

Process water treatment

The term process water covers water that is used in a variety of manufacturing processes, as a raw material, transport medium, coolant, etc.

In many cases the water used is produced by the local waterworks. Since demand can vary it is necessary for some industries to have their own waterworks that will guarantee a regular supply of water. Over certain periods, in summer for example, water demand can rise dramatically for businesses such as the fruit and vegetable trade. Industries that use water for cooling or as feed water also require water with a low alkalinity and hardness. If surface water is used it generally undergoes the same type of treatment as at municipal waterworks. This treatment is a combination of precipitation, in which flocs are separated by sedimentation or flotation, and by precipitation in filters.

Industrial water treatment

Water from many industrial processes is usually so contaminated that it cannot be released directly into a recipient waterway, or, as in many cases, sent to a municipal treatment plant without first undergoing some form of pre-treatment. In some cases the water is recirculated and, if so, generally treated by filtration and precipitation with a metal salt.

In contrast to municipal wastewater, the contaminants that have to be removed vary widely, depending on the type of industry the water comes from. The advantage of treatment at source is that we usually know what contaminants are present in the wastewater and therefore know what has to be removed.

Contaminants in industrial wastewater can include:

Suspended solids
Grease, oils, sand, hydroxides, pigments, fibres, etc.

Oxygen-demanding substances
Phenol, sugar, proteins, etc.

Colours
Pigments, sulphides, organic material

Metals
Cr, Cu, Zn, Ni, Pb, sulphides, etc.

Nutrient salts
Phosphates, nitrogen compounds

One parameter that often requires adjustment is the **pH value**, as many processes involve the use of both acids and bases.

Table 3:14 gives examples of various industries and their respective contaminants and properties that require treatment.

➤ **Table 3:14** Treatment parameters for various types of industries.

Type of industry	Contaminants/problem
Car wash	Oils, SS, oxygen-demanding substances, solvents
Brewery	SS, oxygen-demanding substances, pH, nutrient salts
Fishing industry	Grease, organic material, SS, nutrient salts, odour
Tanning	Heavy metals, odour, sulphides, oxygen-demanding substances, nutrient salts
Mining industry	SS, heavy metals, nutrient salts
Chemical industry	Oxygen-demanding substances, toxins, odour, phenol, nutrient salts
Paint shop	Paint, solvents
Pharmaceuticals manufacture	Oxygen-demanding substances, solvents, nutrient salts, SS
Dairy	pH, grease, organic material
Engineering industry	Oils, heavy metals
Slaughterhouse	Nutrient salts, grease, SS, pH, odour
Steel production/metal manufacturing	Oils, SS, heavy metals
Textile industry, dyeing	Paint, oxygen-demanding substances, odour, SS, heavy metals, oils, solvents

Industrial water treatment methods

There are many different methods of treating industrial wastewater. The method that is chosen depends mainly on what needs to be removed and how much of it needs to be removed to meet the relevant threshold limits.

The following methods are commonly used to treat water in industry:

Mechanical treatment, separation by sedimentation, flotation or filtration
Chemical precipitation
Biological treatment
Membrane filtration
Electrodialysis
Ion exchange
Adsorption using activated carbon

Depending on the required treatment results, the various treatment methods may be combined or used independently to achieve the best results. In general the treatment processes used in industry are much more compact than the methods used in municipal wastewater treatment.

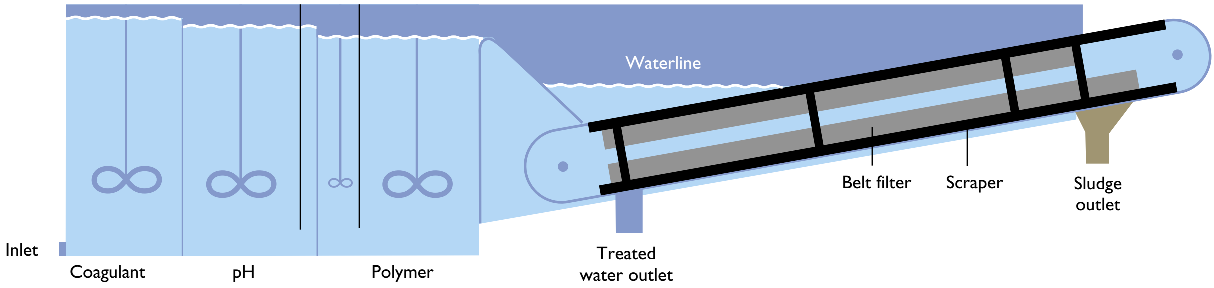
Chemical precipitation

Chemical precipitation can be used to reduce the majority of contaminants that occur in industrial wastewater. All possible variants – including direct precipitation, pre-precipitation, simultaneous precipitation, post-precipitation and precipitation in the filter – are used. Trivalent or multivalent salts such as PIX-110 or PAX-XL60 are often used for precipitation in combination with an anionic polymer to strengthen the flocs. Water from certain industries, such as the textile industry, may be treated using combinations of methods. For example, a metal salt may be supplemented by an organic coagulant that has been specially developed for dye reduction. Chemical precipitation is also frequently followed by lamellar sedimentation or flotation, and more recently by the use of belt filtration. Supplementing chemical precipitation by separation through a belt filter has been shown to considerably reduce the space requirements for a treatment plant.

Belt filtration

Belt filtration is based on various pre-treatment stages followed by an endless belt filter, with a chemical section that is adapted to suit the required retention times and reaction times. These can vary considerably depending on the substances that are to be precipitated and the chemical additives that are chosen. The process is chosen on the basis of completed laboratory trials, which usually leads to a combination of several different process stages, of which there are generally three.

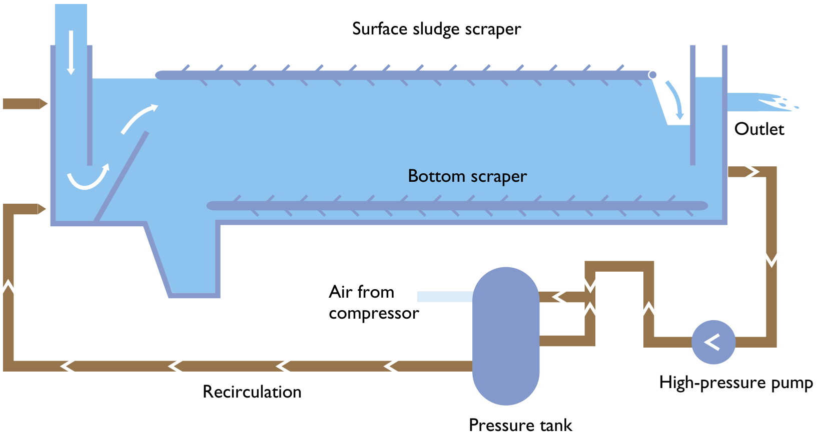
A typical process sequence for a belt filter process consists of pH reduction and the addition of a metal salt in the first chamber. This is followed by neutralisation with the aid of a base in the second chamber, and finally the addition of a polymer to ensure effective coagulation in the third chamber. The flocs that are formed are then removed from the aqueous phase by the subsequent belt filter, on which the sludge is dewatered to give a typical total solids content of 6–10%.



➤ **Figure 3:24** AL-2 belt filter.

Flotation

Separation by flotation generally uses the same chemical processes as used with the belt filter. The belt filter can instead be followed by a flotation plant. The flotation process itself involves adding a mixture of water and air to the chemically treated water. Air bubbles attach themselves to the flocs and lift them to the surface, where they can then be scraped off as a sludge.



➤ **Figure 3:25** Flotation plant.

Biological treatment

Most biological treatment methods that are used in municipal wastewater treatment are also used in industry. The factor that distinguishes some industrial wastewater from municipal wastewater is the lack of nutrient salts in the influent wastewater. Phosphorus and nitrogen must therefore be added separately in order to achieve effective biological treatment.

Biobeds, biotowers and bio-rotors are commonly used for treating high concentrations of dissolved organic material, for example in brewery wastewater. Where treatment requirements are strict, a biobed treatment can be supplemented by an activated sludge stage.

Anaerobic treatment, like that used to digest sludge, is also an alternative for treating very high concentrations of organic material.

Electrodialysis

Electrodialysis is sometimes used for recovering dissolved contaminants, such as metal ions. The method is based on passing the contaminated water through an electric field so that the positive ions are drawn to a negatively charged electrode, or conversely, so that negative ions are drawn to the positive electrode.

Placed between the electrodes are a number of membranes that are permeable to either positive or negative ions. This leads to the concentration of, for example, positive ions in one of the chambers, and their reduction or complete removal from the other chamber.

Ion exchange

During ion exchange the undesirable positive ions in the contaminated water are replaced with other positive ions. An ion exchange unit works rather like a filter that traps ions in an ion exchange medium. The ion exchange unit only removes positive or negative ions. It has a limited capacity and must be regenerated once the ion exchange matrix has become saturated.

Reverse osmosis

If two volumes of water containing different concentrations of salt, for example, are separated by a semi-permeable membrane, then the water will flow from the chamber that has the weaker salt solution to the chamber with the stronger solution. This gives rise to a pressure difference between the two chambers. Eventually this will reach the point where the diffusion of water in both directions is balanced. If the chamber containing the stronger salt solution is pressurised, water can be forced through the membrane. In this way clean water is obtained in the chamber with a low salt concentration, while the salt solution in the other chamber becomes more concentrated.

Adsorption using activated carbon

Active carbon has a very large surface area and pores of varying sizes. This combination of large surface area and pores is used to bind larger dissolved organic contaminants by a process known as adsorption.

Active carbon comes mainly in two forms, as **powder** or as **granules**.

The powder form is added directly to the water requiring treatment, and then precipitates out and is separated. Granulated activated carbon is placed in a filter cartridge through which the contaminated water is forced. Activated carbon has a limited adsorption capacity and must therefore be regenerated after a certain period of use.

Water is one of the most important raw materials in the paper manufacturing process.

Pulp and paper industry

The pulp and paper industry uses large amounts of water and is therefore often based in locations that have an excellent supply of surface water. Water is one of the most important raw materials in the manufacturing process, in which it is used to make chemical solutions, to carry fibres and to wash the pulp.

In the past, fresh water was used in every stage of manufacture and was then discharged straight into the waterways, but today's plants and processes recycle much more water, and therefore have less impact on the aquatic environment.

Environmental efforts have concentrated mainly on treating water at source. This means that, whenever possible, the contaminants must be removed within the process. To achieve the best possible environmental results it is necessary to find the right balance between internal process measures and external treatment. The highest emissions into the water come from the sulphate process, which is also the commonest method of producing pulp. This is an area where processes have also been developed to reduce the environmental burden, such as extended cooking and oxygen delignification, i.e. treating with oxygen in an alkaline environment under high pressure. Bleaching with chlorine gas is now only used by a few pulp mills around the world and has instead been replaced by treatment with chlorine dioxide, ozone, hydrogen peroxide and peracetic acid. The transition to ECF (Elementary Chlorine Free) and TCF (Totally Chlorine Free) bleaching has also made it possible to reuse the water from bleaching plants and reduce water consumption.

Environmentally harmful emissions into water from the pulp and paper industry can be divided into the following main groups:

suspended solids
oxygen-demanding substances
chlorinated organic compounds
chlorates
nutrient salts
metals
pH modifiers

Raw water

Most pulp is produced in countries with a plentiful supply of water.

The pulp and paper industry is a major consumer of surface water, which is also the commonest source of raw water, particularly for pulp manufacture, although groundwater may also be used. The majority of pulp is produced in countries with a plentiful supply of water. Water is naturally recycled to a much greater extent in countries that have poor access to water.

To ensure acceptable water quality, the treatment is adapted to suit the composition of the raw water and the product that is being manufactured. For certain products or applications, such as spray water for internal cleaning, filtration alone may be adequate.

The transition towards increased recycling using newer oxygen-based processes (hydrogen peroxide, ozone, peracetic acid) has led to stricter requirements on water quality in bleaching processes such as ECF and TCF. Treatment is carried out in the same way as for producing potable water in municipal treatment plants, i.e. chemical precipitation. Aluminium salts such as Kemwater ALG and Kemwater PAX are generally used. Iron salts are less common, but are used when the quality of raw water is very poor, due to a high content of humic substances, or when using a decarbonation stage if the pH is high. The equipment that is most commonly used is a flotation basin with sand filter or self-cleaning sand filter.

Water for certain purposes, such as feed water for steam boilers, requires special treatment such as desalination or ion exchange after chemical precipitation and filtration.

The quality of raw water varies during the year, particularly during spring and autumn floods, when the concentrations of humic substances and particles can increase drastically. This can be remedied by adding polymers, particularly the anionic type. Polymers can also be used if a treatment plant has problems due to excessive loading.

Internal treatment

The general strategy of the pulp and paper industry is to treat waste at source, i.e. within the industry, by modifying processes and thereby reducing emissions. Water consumption is now considerably lower than it was just a few decades ago.

➤ **Table 3:15** Water consumption by Nordic pulp and pulp industry.

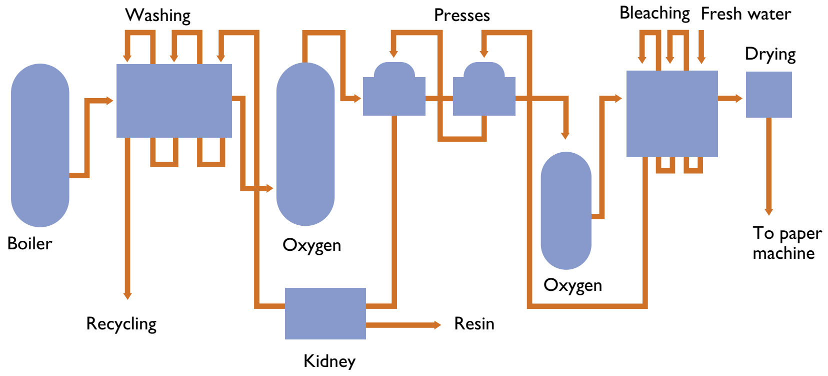
	1970s m³ water/tonne product	2000 m³ water/tonne product
Bleached sulphate pulp	250	20–80
Mechanical pulp	30	10–20
Fine paper	100	5–20

It is mainly the introduction of oxygen delignification, modified cooking and new bleaching methods such as ECF and TCF, that have made it possible to reduce water consumption so drastically. However, it should not be forgotten that this development has also been driven by pressure from authorities and environmental organisations to reduce environmental impact.

In the case of chemical pulp manufacture, the transition to ECF and TCF bleaching has made it possible to recycle more water in bleaching plants. The commonest chemical processes for pulp manufacture are:

Sulphite – acid pulp cooking with hydrogen sulphite/sulfur dioxide
Sulphate – alkaline pulp cooking with hydrogen sulphide/sodium hydroxide

Sulphite plants have been able to recycle their water entirely with the aid of internal treatment using polymers and flotation. Problem substances, such as resin, are coagulated out of the process very efficiently using an "artificial kidney" (NetFloc). The water can be reused in the bleaching plant and the separated contaminants then go on to chemical recovery or are used for energy production.



➤ **Figure 3:26** The NetFloc process.

Sulphate plants produce certain process-disrupting substances that must be eliminated from the process in order to improve the recycling of water. Extensive development work is being done in this area, and a modified internal treatment similar to that for the sulphite process is currently being used at a Swedish sulphate pulp mill that uses TCF bleaching.

Development work is also being carried out in mechanical pulp production in an effort to reduce water consumption, but because this process already operates with less water than the others do, the demand is not so great. Efforts to close the cycle by chemical means are focusing mainly on various types of organic polymer. At present it is not possible to recover chemicals from the process in the same way as in chemical pulp manufacture.

The backwash from paper machines has always been reused in what are known as short and long circulation systems. Short circulation means that the water circulates around the process without being treated, while long circulation means that the water is partially treated before being recirculated. With today's effective retention systems it is rarely necessary to resort to any other treatment other than filtering.

External treatment

The forestry industry has been treating its wastewater using mechanical, biological and chemical methods for many years now. The high water consumption in this type of industry has also meant that most factories have their own treatment plants. The types of installation vary, depending on the emission requirements and the size of the recipient water.

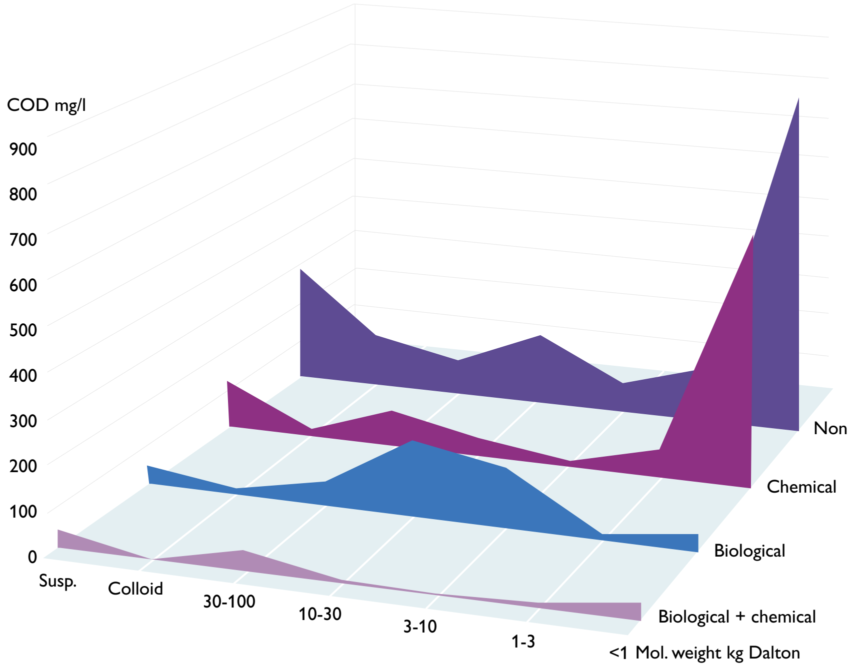
External treatment begins with the primary stage, i.e. some form of mechanical treatment that is primarily intended to remove suspended solids. The commonest method is to use sedimentation basins, but flotation can also be used.

In the case of some heavily contaminated wastewater, chemical precipitation with a metal salt and/or polymer may be used. Chemical precipitation effectively removes substances that are difficult to break down, and so reduces the load on the secondary stage, which is usually biological. The wastewater is detoxified by chemical precipitation, and this reduces problems in the biological stage. Sludge loss from the biological stage is a common problem and can be prevented by adding metal salts to the primary stage.

All types of biological methods are used in the pulp and paper industry, but one method that is specific to the forestry industry is the use of large aerated dams with long retention times. Aeration takes place in one or more earth dams, using surface or bottom aerators. Because of the large volumes and long retention times, up to 20 days, this method is relatively insensitive to variations. The treatment efficiency depends on parameters such as retention time, pH, temperature, sludge quantity and the degree of aeration. The COD reduction efficiency, which falls drastically in winter, varies between 10–50%.

Wastewater from the forestry industry contains small amounts of phosphorus and nitrogen in relation to the amount of organic material. It is therefore necessary to add nutrient salts in some form. Ready-mixed nutrient solutions have been popular in the past, but the current trend is to add phosphorus in the form of phosphoric acid, and nitrogen in the form of urea. It is difficult to determine the ideal dosage, which means that a surplus of phosphorus and nitrogen often remains after the biological treatment.

Chemical precipitation with metal salts is therefore fairly common after biological treatment, especially activated sludge processes. Chemical precipitation reduces phosphorus by more than 90%, as well as reducing nitrogen. Non-biodegradable material (high molecular number) is also reduced in the chemical stage and emissions of suspended solids (SS) fall. Iron aluminium sulphate (Kemwater AVR) is commonly used in the Nordic countries, but iron salts alone may also be used.



➤ **Figure 3:27** Fractionation of untreated and treated water using different treatment techniques. The fractions are SS, colloidal material and dissolved substances with a high molecular weight.

In today’s environmentally aware forestry industry it is increasingly common to use separate treatments for each wastewater fraction. Treatment can then be adapted to suit the individual contaminants in the wastewater. In the case of wastewater from the coating industry, membrane treatment may be an alternative if the coating can be reused. Otherwise, chemical precipitation may be used to remove the particles from the wastewater.

Another wastewater fraction that can be treated separately is the water from screening. This water contains bark particles and substances that can disrupt the biological action in biological plants. Wastewater from the screening process responds well to treatment by chemical precipitation, and can be reused afterwards.

Sludge dewatering

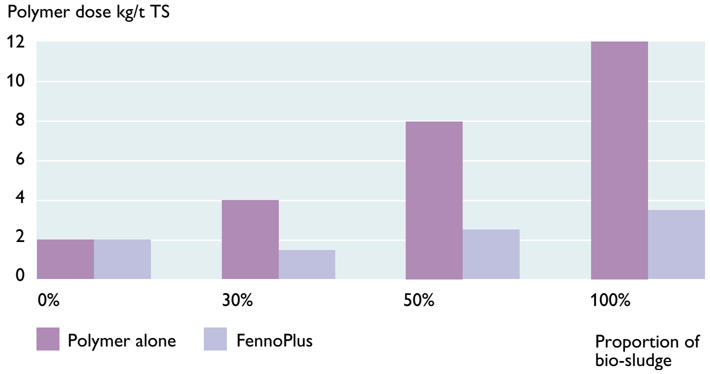
The pulp and paper industry generates large amounts of sludge. This consists mainly of bark, timber processing waste, sludge, recycled fibre waste and deinking sludge. Large pieces of bark and timber processing waste are burned in special bark incinerators, while the rest is recirculated or used as landfill.

The sludge from external treatment is often treated separately, and dewatering may involve several stages, depending on whether the sludge must be burned or dumped.

The incineration of sludge has become more common because of taxes and charges, and the reduced availability of landfill sites. This has also led to greater demand for a higher total solids (TS) content after sludge dewatering.

Primary sludge used to contain a lot of fibre and was mixed with sludge that was difficult to dewater, such as biological sludge, in order to facilitate dewatering. Today's resource-efficient factories produce much less primary sludge, which has made sludge dewatering more difficult, while demands for a higher TS content have also increased. Cationic polymers are most commonly used with mixed sludge (primary sludge and secondary sludge), but since the goal is to achieve higher TS content and more effective dewatering, additional components may be used, such as iron salts, bentonite or organic coagulants. The method of using iron salts with polymer (FennoPlus) for dewatering mixtures of biological sludge gives a better TS content and cleaner reject water. Hydrogen sulphide, which is commonly produced during the dewatering of biological sludge, can be eliminated by adding Fe salts.

Lower polymer dose with FennoPlus system



➤ **Figure 3:28** Comparison of polymer dosage with and without FennoPlus for different proportions of biological sludge.

Textile industry

The textile industry is one of the biggest industrial water consumers, with an average consumption of 20–50 l/kg of fabric produced. Textiles are put through several washing stages to give fabric its desired characteristics. Textile fibres can be divided into two main groups, natural and synthetic, and depending on which group they belong to there are several chemicals and additives that are used in their preparation (see table 3:16). The "average wastewater" from the textile industry contains the following groups of contaminants:

Coloured wastewater is one of the most typical characteristics of almost all types of water from the textile industry.

- **dyes**
- **textile additives**
- **detergents**
- **chemicals**
- **lanolin and oils**
- **traces of textile fibres**

Coloured wastewater is the most typical characteristic of almost all sorts of water from the textile industry. The colour is due to dye residue, i.e. dye that has not been fixed in the textile fibre, and its concentration in wastewater depends on the type of dye and the amount used during the dyeing process. The physical conditions during the dyeing process (such as temperature, pH, etc.) also have a major effect on the concentration of residual dye in wastewater. The disadvantage of these substances is that they colour the water, even in low concentrations. The lowest concentration at which residual dye can be seen in water is around 0,1 mg/l. There is no evidence to show that textile dyes in water have any significant effect on the concentration of organic material in wastewater. The increased concentration of BOD and COD in this type of water is instead caused by textile additives, such as starches, bleaches, foam inhibitors, enzymes, high-molecular organic compounds, etc.

The water that is most heavily contaminated in environmental terms comes from washing wool, which contains large amounts of organic material (lanolin) and minerals. As a result, the wastewater contains large amounts of BOD, COD and SS, which make it difficult to treat. This type of wastewater is very common in the UK, New Zealand and South Africa – countries that breed large numbers of sheep.

➤ **Table 3:16** Average concentrations of contaminants in various types of textile wastewater.

Pre-treatment	COD (mg/l)	BOD_5 (mg/l)	SS (mg/l)	pH
Animal fibres (wool washing)	50 000–150 000	20 000–60 000	5 000–20 000	7–8,5
Plant fibres (linen and cotton)	1 500–5 000	300–1 000	100–500	7–10,0
Water from dyeing	150–1 500	150–500	30–300	5–9,5

Basic methods for treating wastewater from the textile industry

Chemical treatment

Chemical treatment (precipitation) is widely used for treating wastewater from the textile industry. Chemical treatment involves adding a coagulant to precipitate out dissolved substances in the water and then remove them as a sludge. Some particulate substances are also bound to the flocs that are formed when the coagulant is added. The sludge is separated by sedimentation or flotation. Organic flocculants, polymers, are generally added in dosages of 0,1 to 1,0 mg/l to encourage separation of the sludge.

The main advantage of using chemical precipitation is the efficiency of dye reduction – especially for dyes that are insoluble in water, where a reduction efficiency of 85% can be achieved. On the other hand this method is not especially effective for water-soluble dyes. Reactive dyes remain in the water after chemical treatment, which means that the water remains coloured.

Coagulants that are used for the treatment of textile wastewater include iron(II)sulphate in combination with lime, iron(III)salt (Kemwater PIX) and aluminium sulphate (Kemwater ALG). Organic cationic polymers have recently been developed especially for dye reduction (Kemwater Optifloc). These products remove soluble and reactive dyes by forming insoluble compounds that can be separated by sedimentation.

Table 3:17 Chemical treatment efficiency.

BOD_5 (%):	min.	30
	max.	60
	average	45
COD (%):	min.	35
	max.	70
	average	55
Dye reduction (%)	min.	75
	max.	95
	average	85

Choosing the right coagulant and the right dosage is very important. The pH of the wastewater is also very significant. The optimum pH range for precipitation with aluminium salts is between 5 and 7, while iron salts can be used in the range 5–11. If the alkalinity of wastewater is low it is better to use iron sulphate in combination with lime.

One good way of improving treatment efficiency for heavily contaminated water, such as that from the wool industry, is to use anaerobic fermentation (digestion) before the chemical treatment stage.

Biological treatment

Biodegradability tests have shown that most textile dyes and some high-molecular additives are either non-biodegradable or biodegrade very slowly in a normal biological treatment process, i.e. the activated sludge method. Dye reduction is not particularly high, only around 50%. Some dye reduction can be achieved under anoxic conditions. In general, the activated sludge process gives a reduction of between 80 and 90% in BOD_5 but the retention time at this stage must generally be longer than a day. In most cases phosphorus and nitrogen must be added, since these elements are in low concentration in textile wastewater. Better treatment results are often obtained if wastewater from the textile industry is led to a municipal wastewater treatment plant for treatment. Some parameters can however have a negative effect on the biological treatment stage if they are neglected. These include pH, temperature and the concentrations of detergents, heavy metals, sulphides and chlorides.

The textile industry uses large volumes of water and therefore requires efficient water treatment methods.

Example where wastewater from the textile industry is treated at a municipal plant

The mill in question manufactures cotton fabric, and the water discharged from the dye works and pre-treatment stage is 1500 m^3/day. The water, which contains sulphur-based dyes, is normally intensely coloured, and the concentrations of the various contaminants can be regarded as average according to table 3:16. The water is discharged into the sewer and diluted at the treatment plant with wastewater, which gives a total flow of 10 000 m^3/day, equivalent to a load of 80000 person equivalents. The concentration in the activated sludge basin is 7–10 kg SS/m^3 and the retention time in this basin is 10–14 hours.

➤ **Table 3:18** Treatment results for municipal treatment plant taking wastewater from dye works.

Parameter	Influent	Effluent	Treatment efficiency (%)
COD (mg/l)	600–1000	60–110	90
BOD_5 (mg/l)	300–500	8–15	98
SS (mg/l)	100–300	10–15	94
pH	7,5–9,5	7,2–7,5	
P_{tot} (mg/l)	3–7	<0,5	<90
N-NH_4 (mg/l)	15–25	0,5–2,5	90
Dye reduction			85–90

Conclusion

Because water is a very important factor in textile production it is essential to find effective techniques for treating the resulting wastewater. It is not possible to treat this wastewater in a single stage, and in some cases chemical and biological treatment must be supplemented by activated carbon filters, oxidation, filtration, etc., to achieve the desired treatment efficiency. In order to choose an economically sustainable and relatively uncomplicated treatment process for water from a given process it is important that we first determine the concentrations of dyes, chemicals and textile additives in the water.

Slaughter industry

Wastewater from the slaughter industry is easy to treat chemically by adding an iron coagulant in combination with an organic polymer, such as polyacrylamide. The coagulant removes larger suspended particles, fats, colloidal particles, proteins and some dissolved organic substances. The commonest method of separating sludge is by flotation, since the nature of the sludge makes it suitable for this method.

In order to achieve satisfactory treatment results it is important to have the right pH during the precipitation stage. The optimum pH when the coagulant is added is around 5. After a few seconds the pH should be raised to between 6 and 6,2 to achieve optimal coagulation.

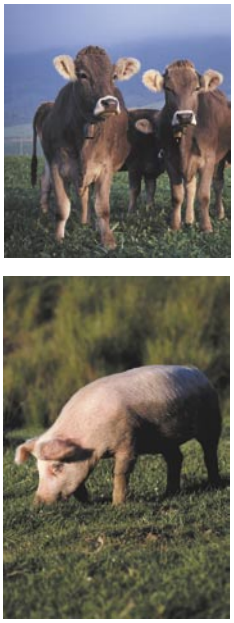
Generally the treatment efficiencies achieved are around 85% COD, 70% nitrogen and 95% phosphorus. The concentration of coagulant that needs to be added depends on the degree of contamination of the wastewater.

➤ **Table 3:19** Typical treatment results for chemically treated wastewater from the slaughter industry.

Parameter	Treatment efficiency
COD	85%
Nitrogen (N_{tot})	70%
Phosphorus (P_{tot})	95%

Chemical precipitation is a very reliable and compact process, which means that it requires less land space to construct a treatment plant. If a higher treatment efficiency is required than can be achieved by direct precipitation then it is easy to add a traditional activated sludge stage as the final treatment stage.

The processing of sludge is often perceived as a problem – not unlike the issue of wastewater treatment on the whole. The method that is chosen for sludge treatment is often linked to local regulations.



The commonest method of separating sludge from the slaughter industry is by flotation.

Wash water from the freight industry can come from cleaning tankers, railway wagons, lorries or ships.

Wet oxidation is a relatively expensive process, while digestion is an attractive alternative thanks to the methane gas that is generated during the digestion process. This methane can be converted to energy and utilised by the treatment plant. One disadvantage of digestion is the high concentration of nitrogen that builds up in the reject water, which can inhibit the process.

Conclusion

Wastewater from the slaughter industry can be simply treated with the aid of chemical precipitation. One important factor during the treatment process is the pH level.

The resulting sludge can be processed in a variety of ways, the choice of which usually depends on local conditions and requirements regarding the final quality of the sludge.

Treatment of industrial wash water

This water may have been used for washing tankers, rail cars, lorries or boats. Because these vehicles can carry everything from foodstuffs to toxic substances, such as methylisocyanate or phenols, it is clear that special treatment is required for tankers.

In general, we must distinguish between wastewater (wash water) that comes from **sea freight** and that which comes from **land freight**.

In accordance with the Marpol I and II* agreements, wastewater that comes from **sea freight** must be taken care of in ports that are specially equipped for this purpose. As a rule this water is not heavily contaminated, and consists basically of wash water and ballast water. It does sometimes contain considerable amounts of oil however.

The wash water that comes from cleaning tanks that are used for **land freight** contains a much wider range of substances and is normally highly concentrated. This type of wash water can be divided into four main groups:

- **dispersions**
- **oils and greases**
- **biodegradable wash water**
- **toxic wash water**

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* The Marpol convention is an international convention for preventing pollution from shipping. This International Maritime Organisation (IMO) convention was adopted in 1973 and updated in 1978. Marpol was set up with the aim of controlling and minimising intentional, negligent or accidental discharges of oil and other substances from shipping into the marine environment. Many additions have been made to the convention, although several have not yet come into force.

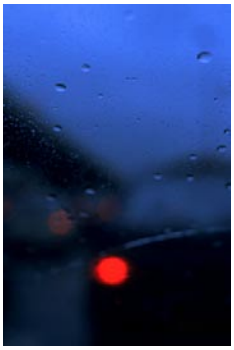
Rules that govern the various possible sources of discharges from shipping are gathered in five appendices. Marpol I and II are contained in appendices I and II.

Appendix I sets out the rules for minimising oil discharges caused by shipping, in particular oil tankers. Appendix II contains the rules for sea freight and unloading of chemical products.

➤ **Table 3:20** Average contaminant concentration in various types of wash water.

	COD (mg/l)	BOD (mg/l)	SS (mg/l)	pH
Wash water, land	3000–30 000	1 000–15 000	500–3 000	4–10
Wash water, sea	500–10 000	200–5 000	200–2 000	4–10

Tvättvatten från biltvättanläggningar innehåller tungmetaller och oljor/fetter.



Basic methods for treating wash water

Pre-treatment and buffering

Pre-treatment is the first process stage in the treatment of wash water. This stage consists of filtering the water through screens or a rotating sieve and three-stage sedimentation by gravitation, to separate oil, grease, primary sludge and water.

The pre-treated water is buffered before it moves on to the chemical treatment stage. Often a system of two buffering basins is used, one for the treatment itself, and the other as an equalisation stage. This makes it easier to determine the optimum dosage of coagulant to match the degree of contamination of the water.

Chemical treatment

Chemical treatment is used to remove dispersions, suspended solids, heavy metals, oil and organic solvents that are insoluble in water. There are two main mechanisms in this stage:

destabilisation of colloidal matter through charge neutralisation
reduction of metal complexes through precipitation

The general mechanisms behind these reactions are described in more detail in chapter 7.

Common coagulants are iron and aluminium salts, such as trivalent iron chloride, iron chloride sulphate and polyaluminium salts, in combination with organic flocculants, usually polyacrylamides, to improve sludge separation characteristics.

Because of the relatively high oil content in the sludge, flotation is the preferred method of separation.

Since the pH level of the influent wastewater varies widely it is recommended that the pH is adjusted before adding the coagulant. The optimum pH for precipitation with aluminium coagulants is, as mentioned earlier, between 6 and 7,5, while iron coagulants work well between a pH of 5 and 9,5. The larger pH range for iron coagulants is an advantage, particularly when precipitating heavy metals.

With strongly basic aluminium salts the water can be treated within roughly the same pH range as for iron salts.

Iron and (poly)aluminium salts can, for example, be used to precipitate:

- **suspended solids**
- **dispersed particles**
- **dispersed fat**
- **emulsified oil or solvents that are not soluble in water**
- **dissolved charged substances, e.g. phosphates**
- **heavy metals**

Flotation is preferably used for sludge that contains grease or oil.

Page 188 gives more information on how pH affects the precipitation of heavy metal ions.

Anionic polyacrylamides are often used to improve the strength of flocs and their precipitation rate. (See pages 203–204.)

➤ **Table 3:21** Efficiency of chemical treatment of wash water.

Parameter	Treatment efficiency
BOD (%)	min. 10 max. 60
COD (%)	min. 20 max. 60
SS (%)	min. 60 max. 90

Biological treatment

In order to remove biodegradable material a biological treatment stage, such as an activated sludge stage, is used. Because the wastewater can contain a large proportion of materials that degrade very slowly, such as ethyl benzene and toluene, it is preferable that the biological treatment stage has a low sludge load. A guide figure for sludge load is that it should be between 0,05 and 0,1 kg BOD/kg SS per day. Trials using membrane technology have shown promise in treating the mainly organic contaminants that are encountered here.

Wash water is distinguished by its high COD/BOD ratio after treatment. This is a sign that the wastewater contains high concentrations of COD that does not degrade readily.

The activated sludge often has a limited ability to form flocs as a result of the varying composition of the water. This often means that the effluent water has a high concentration of suspended solids. It is therefore advisable to have a third treatment stage, such as a sand filter, or flotation, to separate these substances.

➤ **Table 3:22** Efficiency of biological treatment of wash water.

Parameter	Treatment efficiency
BOD (%)	min. 50 max. 90
COD (%)	min 20 max. 70
Total N (%)	min. 20 max. 90

Conclusion

Large amounts of water are used for the treatment of wash water. Because of the diversity of this wash water it is extremely important to be able to use multipurpose treatment techniques, such as chemical precipitation and activated sludge treatment.

Because clean water is becoming an increasingly scarce resource in our society it will become necessary in the future to find methods that make it possible to reuse wash water. Likely methods include evaporation and membrane filtration.

Chapter 4

Sludge

Chapter 4 Sludge

Sludge

”Don’t throw out the dirty water until you have some clean.”

The purpose of water treatment is to separate undesirable substances from the water. This is done by encouraging dissolved substances and small particles to form larger particles that can be separated. When these larger particles clump together they form a sludge. Sludge can be defined as a mixture of particles and water. The total solids content can be high or low, and the content will vary depending on the source.

Sludge generally contains both useful and useless components. It is because these are mixed together that sludge is often classed as waste. But sludge is actually a resource; industrial sludge can contain valuable metals, waterworks sludge can contain precipitation chemicals, and sewage sludge contains nutrients. All these useful constituents may be lost if sludge is classed as waste. We must instead regard sludge as an opportunity rather than a problem.

■ Waterworks sludge

The aim of potable water production is to separate undesirable substances from the water. Examples of such substances are clay and mineral particles, algae and humic substances (which were discussed earlier in chapter 2).

These contaminants are separated as aqueous sludge, which can be difficult to dewater. When the treatment includes a chemical stage (coagulation and flocculation) this also produces a hydroxide sludge (chemical sludge) that can be bulky and may also be difficult to dewater.

➤ **Table 4:1** Estimated sludge production in Sweden.

Sludge type	Vol. treated water (Mm³/year)	Total sludge weight (tonnes DS/year)	Sludge weight per m³ treated water (g DS/m³)
Groundwater treatment	328	1 000	3
Surface water treatment	466	10 000	22

Source: Publication VAV P67, Sep. 1990, "Vattenverksslam" (Waterworks sludge).

It can be seen from the table that surface water treatment plants make the main contribution to sludge production during potable water production. As a guide figure, the sludge contribution from surface water treatment is around 8,5 g DS per person per day.

So what happens to this sludge from potable water production? There are two chief alternatives: return it to the water source or transfer it to the sewage system.

The negative consequences of returning the sludge to the water source is the bank of sludge that builds up around the discharge area and the clouding of the water, which can have a negative effect on the ecosystem in the waterway.

Table 4:2 shows the average composition of sludge from 11 surface water treatment plants.

Table 4:2 Precipitation with aluminium salt.

mg/kg DS									% of DS			
As	Cd	Cr	Co	Cu	Hg	Ni	Pb	Zn	P_{tot}	N_{tot}	Al	Fe
7,4	0,18	37	3,7	64	0,16	19,9	18	91	0,11	1,5	17,4	1,4

Source: Publication VAV P67, Sep. 1990, "Vattenverksslam" (Waterworks sludge).

The content of nitrogen and phosphorus contaminants is low, around 1,5% N and 0,11% P (calculated as % of DS).

Sewage sludge

During the various treatment stages the contaminants are converted into such a form that they can be separated by means of suitable separation methods. The contaminants are separated as aqueous sludge, which must be processed in the way that is most technically, economically and environmentally appropriate. The nature of the sludge, its properties and volume will vary from place to place, in the same way as wastewater.

The costs of processing sludge are often considerable. It can also be difficult to find a good method of final disposal. If carried out correctly, the processing of sludge is one of the most important stages in wastewater treatment.

Sludge is processed in stages that comprise a sequence of operations such as thickening, stabilisation and dewatering. Composting, incineration, dumping or use as a soil improver are the commonest methods for final disposal of sludge.

Various types of sewage sludge

The sludge that is separated during treatment is usually referred to as raw sludge. In order to make it biologically stable the raw sludge must undergo further treatment.

Depending on which stage of the process the sludge is removed from, it may be known as:

Primary sludge from the mechanical treatment stage

Secondary sludge or biological surplus sludge from the biological treatment stage

Tertiary sludge or chemical sludge from the post-precipitation stage

The approximate quantities of sludge are shown in the table below.

➤ **Table 4:3** Approximate quantities of sludge produced during different treatment processes and treatment stages when Al^{3+} and Fe^{3+} are used as coagulants.
The amounts refer to unstabilised sludge.

Sludge quantity from treatment	g/p•d	% DS after thickening	Volume l/pe
Post-precipitation			
Primary sludge	50	6	0,8
Secondary sludge	30	2	1,5
Tertiary sludge	25	2	1,2
Mixed sludge	105	3	3,5
Pre-precipitation			
Primary sludge	110*	5	2,2
Secondary sludge	10	2	0,5
Mixed sludge	120	4	2,7
Direct precipitation			
Primary sludge	110	5	2,2

* Of which 25 g/p•d consists of metal hydroxides and phosphates.

Reject water

Reject water is produced whenever sludge is thickened or dewatered. It is normally returned to the first treatment stage in the treatment plant. Because reject water increases the load on the treatment process it is important that it is as free from contaminants as possible. Otherwise the internal load imposed by reject water can be considerable.

Sludge composition

Sludge can be said to contain two main components: liquid and solids. Because of the gelatinous nature of sludge these two components cannot be separated from each other easily.

The liquid consists of water and substances dissolved in it. These may be inorganic salts, such as ammonium, and organic substances such as carbohydrates and fatty acids. When the sludge is dewatered these dissolved substances remain in the liquid. As the dry content of the sludge increases so does its gelatinous nature. The solid substances surround themselves with compounds that have a strong affinity for water (hydrophilic system). To ensure successful dewatering these gel-forming substances must first be destroyed, for example by hydrolysis (aerobic stabilisation, digestion, thermal or chemical treatment) or by adding chemicals such as polyelectrolytes that interfere with the geometry of the gel-formers.

Sludge from wastewater treatment

All types of sludge, whether organic or inorganic, consist of a solid phase with a certain amount of liquid. The properties of this liquid are often assumed to be similar to that of "common" water. However, this water has different physical properties within the sludge particles, and these properties affect the dewatering and separation characteristics of the sludge. The liquid phase in a sludge floc cannot be said to have the same physical and chemical properties as normal water. Over the last few years several researchers have developed the following descriptions of the various physical properties of the liquid phase in sludge.

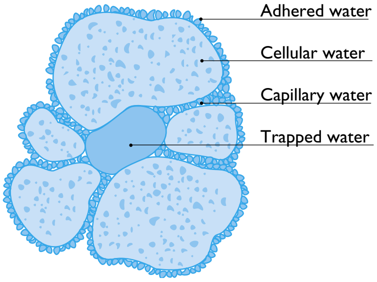
Free water: water that is not bound to the particle in any way

Capillary water: mechanically bound water in sludge particles

Adhered water: physically bound layer of water molecules that adhere to the surface of sludge particles by means of hydrogen bonds

Chemical: Strongly bound water to metal ions

Cellular: Water inside cell walls

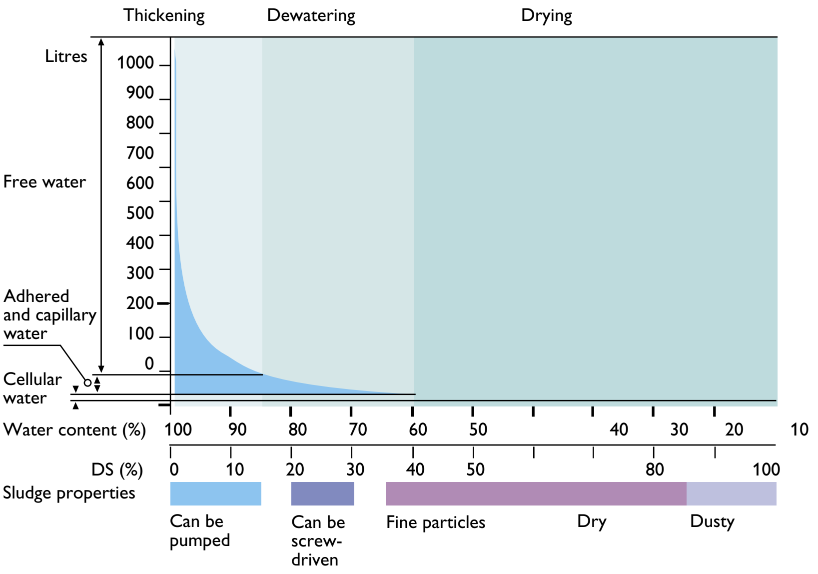


➤ **Figure 4:1** Distribution of water in a sludge particle.

Figure 4:1 shows how the various water phases are associated with sludge particles.

Using current dewatering technology it is generally only possible to remove a certain proportion of free, adhered and capillary water. Factors that interfere with the dewatering of sludge are:

- **High sludge age during nitrification and denitrification, which leads to higher shear forces on particles.**
- **The hydrophilic properties of metal hydroxides that are formed during chemical phosphorus reduction.**
- **The gelatinous nature of sludge that develops during biological phosphorus reduction.**
- **The improved initial separation stage in treatment plants (better screens) that remove larger particles and fibres, which results in smaller particles later on in the process.**
- **Reduced retention time during anaerobic digestion due to higher load and lower DS contents in sludge entering the digester.**



➤ **Figure 4:2** Liquid distribution in sludge.

Figure 4:2 shows the weight and volume reductions for 1000 litres of sludge when the water content is reduced. The normal DS contents for dewatered and digested sludge are between 18 and 35% depending on the characteristics of the sludge. Even higher DS contents can be achieved in some circumstances.

Water content

The properties of sludge change markedly with its water content, which can be divided into two main types: external liquid and internal liquid. Internal liquid includes internal capillary liquid and cellular water. This liquid is bound to particles in such a way that it is difficult to remove mechanically.

In order to release internal liquid and allow mechanical dewatering it is necessary to destroy the cell walls, for example by aerobic or anaerobic stabilisation, heating or freezing.

External fluid includes absorption liquid, adhesion liquid, contact liquid, capillary liquid and pore liquid.

The liquid that is present in the pores and is affected by capillary forces is known as pore capillary liquid. The quantity of liquid is determined by the size of particles, their geometry and how closely they are packed together. The pore liquid is unaffected by forces from sludge particles.

The pore water can be separated by thickening. Capillary liquid, contact liquid and adhesion liquid can be partially separated by mechanical dewatering. Internal cell liquid can be separated by drying and freezing.

Solid particles

These particles or suspended solids consist of the particles that accompany the wastewater to the treatment plant, microorganisms that are produced in the treatment plant, and metal hydroxides and metal phosphates from chemical precipitation.

Organic substances

Sludge consists largely of organic substances. These consist of microorganisms, their decomposition products and contaminants that have been broken down to varying degrees.

The loss on incineration and degree of mineralisation are two measures of the proportion of organic material.

Organic substances can also include disease-causing organisms known as **pathogens** that come from infected people and animals. These **pathogens** may be bacteria, such as salmonella, or parasites, in the form of worm eggs and viruses.

New analysis methods have made it possible to identify organic environmental toxins more accurately. This means that some completely new parameters will be introduced in the future. Many wastewater treatment plants already analyse for the concentration of chlorinated hydrocarbons.

Inorganic substances

The nitrogen and phosphorus content of sludge is very important with regard to plant nutrition.

The heavy metal content must be carefully controlled. The Swedish Environmental Protection Agency (SNV) has set guidelines for the concentrations that can be tolerated in agricultural use. If a single value exceeds limits briefly and by a small amount it should not restrict the usefulness of sludge.

➤ **Table 4:4** Guide values for heavy metal concentrations in sludge.

Metal		SFS 1993:1271 mg/kg DS
Lead	Pb	100
Cadmium	Cd	2
Copper	Cu	600
Chrome	Cr	100
Mercury	Hg	2,5
Nickel	Ni	50
Zinc	Zn	800

Sludge processing methods

For reasons of economy and hygiene, sludge must undergo various types of processing, such as thickening, stabilisation and sanitisation.

Bildtext!

Sludge thickening

Wastewater treatment produces a thin sludge that consequently has a large volume. Of the total costs of a treatment plant, around 40–60% go toward processing sludge, despite the fact that the volume of sludge is only around 1% of that of the influent wastewater.

In order to reduce the volume and cost of processing sludge it is thickened by sedimentation or flotation before stabilisation and dewatering.

The choice of thickening method depends on the nature of the sludge. Primary sludge is best thickened by sedimentation. In the case of chemical and biological sludges, flotation may be a more suitable method.

Thickening by sedimentation is often carried out in circular basins with a depth of 2,5–5,5 metres that are equipped with surface and bottom stirrers, as well as gate agitators.

➤ **Table 4:5** Sludge load for various types of sludge, for sedimentation by thickening.

Sludge type	Sludge load kg DS/m^2/d
Primary sludge	**100 – 150**
Secondary sludge	**25 – 30**
Tertiary sludge	**25 – 30**
Mixed sludge	**30 – 50**

Flotation thickening tanks are circular or rectangular. Rectangular tanks are considered to be easier to scrape and are therefore more common. The sludge load is140–240 kg DS/m^2•d.

I rötkammare krävs god omrörning för att upprätthålla jämn temperatur och jämt pH.

Stabilisation

Raw sludge contains biodegradable compounds and will therefore remain biologically active until it has been stabilised. To avoid problems, decomposition should be speeded up by digestion, aerobic sludge stabilisation, composting, thermal or chemical oxidation, incineration, pyrolysis or liming.

Sludge digestion

Digestion is an anaerobic process and has been used for many years to produce a sludge that neither smells nor causes other problems when dumped as landfill. It also greatly reduces the volume of sludge.

The decomposition process in a digester has several stages. First, the carbohydrates, fats and proteins are hydrolysed with the aid of enzymes to produce sugars, fatty acids and amino acids.

These are converted into alcohols and simple fatty acids and finally, methane gas and carbon dioxide.

Methane is less soluble in water than carbon dioxide. The gas that is given off therefore contains more methane than carbon dioxide, which remains in the aqueous phase. Digester gas therefore contains around 70% methane and 30% carbon dioxide.

Digestion is carried out in digesters, with retention times of between 15 and 30 days. The temperature is normally kept between 30 and 40°C (mesophilic digestion). Digester systems that work at higher temperatures are also possible (thermophilic digestion). With thermophilic digestion the retention time can be reduced by half.

Digestion is normally an uncomplicated process, although the risk of acid fermentation has to be considered. In unfavourable conditions the first stage of the digestion process can run away. This leads to an excess of fatty acids, which causes the pH to drop sharply and the digestion process comes to a halt.

The normal load of a digester is around 1,5 kg of organic matter per day per m^3.

During digestion the concentration of organic compounds in the sludge falls by 40–60% while the concentration of inorganic material remains unchanged.

The sludge from a conventional treatment plant that uses biological treatment produces around 30 litres of digester gas per person per day, while the quantity of sludge is reduced by about 35%.

➤ **Table 4:6** Volume requirements for digesting various types of sludge.

Sludge	Digester volume l/pe
Primary sludge	30
Primary sludge + biobed sludge	45 – 60
Primary sludge + surplus sludge	60 – 90
Primary sludge, direct or pre-precipitation	70 – 100

The decomposition of organic matter can be described in terms of the degree of decomposition using the formula:

$$a = 1 - \frac{GR_i \cdot GF_u}{GR_u \cdot GF_i}$$

a = degree of decomposition

GR_i = raw sludge ash residue, % of DS

GR_u = digested sludge ash residue, % of DS

GF_i = raw sludge loss on incineration, % of DS

GF_u = digested sludge loss on incineration, % of DS

The sludge that is obtained from pre-precipitation contains considerably more organic material than sludge from a conventional plant. The volume of gas that is produced by digesting this sludge will therefore be higher.

➤ **Table 4:7** Gas production from the digestion of various types of sludge.

	g/p•d	GF(%)	g GF/p•d	Gas production l/p•d
Biological treatment				
Primary sludge	50	75	38	
Secondary sludge	30	70	21	
Mixed sludge	80	74	59	30
Pre-precipitation				
Primary sludge	110*	60	66	
Secondary sludge	10	70	7	
Mixed sludge	120	61	73	40

*) Of this, 25 g is in the form of metal hydroxides and phosphates that do not produce any gas.

Aerobic sludge stabilisation

One alternative to stabilising sludge by digestion is to use aerobic sludge stabilisation. In this process the sludge is aerated for around 15 days at a sludge temperature of 15°C. At temperatures lower than this the aeration time should be extended.

During aerobic stabilisation the organic matter is oxidised. This is followed by oxidation of the nitrogen compounds that are present. It is estimated that these oxidation processes require 1,5–2 kilograms of oxygen per kilogram of organic matter that is introduced.

Stabilisation with lime

All biological activity effectively comes to a stop if the pH rises above 11. This fact is exploited in lime stabilisation, which involves adding enough lime to the sludge to ensure that the pH stays above 11 even after holding for around 14 days.

Stabilisation with lime has several advantages. The process is easy to control, and the investment costs are modest. The phosphates and heavy metals that are present in the sludge are bound very securely by the lime, and pathogenic microorganisms are killed effectively. In order to reduce the internal nitrogen load the high pH of the sludge can be exploited for the process known as ammonia stripping.

Lime may be added to the sludge before or after dewatering. If the lime (slaked lime) is added before dewatering it results in a sludge that is odourless and has much better dewatering characteristics. If the lime (unslaked lime) is added after dewatering it causes a sharp temperature rise in the sludge. This high temperature also pasteurises the sludge.

The disadvantage of this process is its high operating costs.

➤ **Table 4:8** Amounts of lime required for sludge stabilisation.

Sludge type	Amount of lime kg $Ca(OH)_2$/tonne DS	 kg CaO/tonne DS
Primary sludge	**100–150**	**70–120**
Primary + secondary sludge	**300–500**	**200–400**

Thermal sludge processing

Thermal sludge processing refers to processes in which pressurised sludge is subjected to high temperature.

The purpose of thermal sludge processing is, like all other types of sludge processing, to stabilise the sludge, remove water and kill pathogenic organisms.

What happens when sludge is thermally processed is not precisely clear. Many scientists believe that the layer of water that is bound to the surface of particles becomes thinner because of its reduced viscosity. Fats and oils can also be dissolved during thermal processing and this undoubtedly affects dewatering characteristics. The fact that the cell walls of organic particles and organisms are ruptured, thereby releasing their cellular water, also improves dewatering characteristics. And finally, extracellular polysaccharides that bind water, rather like polymers, are also broken down and improve dewatering characteristics.

The microorganisms that make up most of the organic component of sludge consist mainly (with the exception of water) of proteins, carbohydrates and fats. These are normally difficult to break down.

In many countries sludge must be pasteurised before it can be spread on the land or dumped in landfill sites.

Other thermal processing methods

Drying and incineration

In locations where the local conditions make it impossible to dump sludge or use it in some other way, one alternative may be incineration. The calorific value of sludge is around 10–20 MJ/kg of DS. This means that dewatered sludge (DS 25%) cannot normally be incinerated without an auxiliary fuel. To permit incineration without an auxiliary fuel the DS content must be around 40%.

During incineration the air supply and temperature must be carefully monitored to ensure complete combustion. If combustion is incomplete it can lead to odour problems and high emissions of pollutants such as oxides of nitrogen.

Pyrolysis

Pyrolysis is another alternative for using sludge, since it results in oil-like products. During pyrolysis the dried sludge is heated to 300–500°C in an environment that has a poor supply of oxygen and is allowed to carbonise. This produces tar, oil and carbon. The oil yield from trial plants has been 16–30% of the organic content. Some financial support is obtained from the sale of oil products and the costs of dumping are lower than for conventional dumping.

Pasteurisation

In many countries sludge must be pasteurised before it can be spread on the land or dumped in landfill sites. One method of pasteurisation is to heat the sludge to at least 70°C for 30 minutes.

Composting

Composting involves biological thermal oxidation, and is carried out by microorganisms. During composting the sludge reaches a temperature of around 70°C, which kills pathogenic organisms. The sludge is broken down to give a stable end product with a soil-like consistency and odour.

One of the disadvantages of composting is that the “compost heap” must have a dry content in excess of 45%. This means that the sludge must be mixed with a dry biodegradable material, such as sawdust or refuse. The compost must also be mixed and ventilated regularly to supply oxygen and allow carbon dioxide to escape. Without such ventilation the composting process would quickly come to a halt. The process takes several months and therefore requires a lot of space. The resulting compost is very porous, which means that transport costs are high.

Dewatering of sludge

Sludge contains between 93 and 98% water. Its volume can therefore be greatly reduced by dewatering, which is normally what is done. Dewatering can be carried out on stabilised or unstabilised sludge, and the methods that are used are:

- **Drying on a sludge bed**
- **Centrifuging**
- **Filter press**
- **Sieve belt press**
- **Vacuum filter**
- **Screw press**

Torkning på slambädd.

Sludge conditioning

The microorganisms that make up the bulk of sludge surround themselves with a jelly-like layer. This layer attracts water very strongly. It is thought that the microorganisms use this jelly partly as a nutrient store, and partly to protect them from infections and drying out. When sludge is dewatered it must be processed or "conditioned" to break down this jelly layer. This releases the water so that it can be separated using one of the methods described above.

Slamcentrigugering.

The usual method is to add a conditioning agent, whose main task is to improve the dewatering characteristics of the sludge. The conditioning agent also has to restrict the fine particle content of the reject water.

Chemical oxidative conditioning

Kemicond (Kemira's sludge conditioning process) is a chemical-physical conditioning process developed for digested sludge containing iron and phosphorous.

The sludge is acidified straight from the digester in order to dissolve ferrous salts and phosphate at a pH of between 3 and 5. By oxidising the dissolved ferrous salts to ferric salts using hydrogen peroxide, a very strong oxidative environment can be created. The sludge will be disinfected and free from odour.

The oxidised iron will precipitate the dissolved phosphorous in a crystalline form. The sludge's water-retentive gel structure is broken down and the dewatering properties of the sludge are significantly improved. More than 40% TS can be achieved in a screw press.

Iron chloride and lime

A combination of iron chloride and lime has long been used as sludge conditioning agent. This method is suitable for vacuum or filter press dewatering. The consumption of iron chloride and lime is roughly 50 kg/tonne of DS and 100–200 kg/tonne of DS respectively.

Organic polymers

The water-retaining ability of sludge can be greatly reduced by adding organic polymers or polyelectrolytes. There are three different types:

• active cationic	**(positively charged)**
• active non-ionic	**(neutral)**
• active anionic	**(negatively charged)**

The effect of these polymers on the sludge is to bind it together and increase its mechanical strength. Binding together the fine particles and larger aggregates in the sludge results in a large proportion of easily dewatered pores. The increased mechanical strength allows the sludge to withstand the mechanical processing that dewatering involves.

Different polymers exhibit widely differing effects on different types of sludge. Choosing the right chemical is therefore very important. For example, with primary sludge and biological sludge a cationic polymer is very effective, while a purely chemical sludge often gives better dewatering results with an anionic polymer. The most appropriate dewatering polymer can only be chosen after careful testing of the sludge in question.

Polymer consumption varies between 2 and 5 kg per tonne of DS.

Sludge hydrolysis

In certain biological nitrogen reduction processes there is a need for a source of carbon. The denitrification bacteria use this source of carbon to help convert nitrate into nitrogen gas. The carbon source must exist in a form that is easily accessible to the bacteria, firstly in dissolved form, and secondly as short-chain compounds, such as the organic material in treated, precipitated water.

The source of carbon can be obtained by hydrolysing sludge. This can be done **biologically**, with **enzymes**, **thermally** or **chemically**.

Biological hydrolysis is usually known as acid fermentation, and if the process is carefully regulated it can produce fatty acids that denitrification bacteria can use very effectively.

Enzyme hydrolysis involves adding enzymes to the sludge. High temperatures speed up the rate of decomposition, and if the temperature exceeds 60–70°C it prevents the bacteria from consuming the short chain compounds that are formed.

In thermal hydrolysis the sludge is subjected to high temperature, 130–190 °C, which makes the sludge coagulate and breaks down the jelly layer. The proportion of dissolved organic substances is increased.

Chemical hydrolysis involves adding alkali (alkaline hydrolysis) or acid (acid hydrolysis) to the sludge. Suitable alkalis are sodium hydroxide, soda or lime. In the case of acid hydrolysis either sulphuric acid or nitric acid may be added. There are good opportunities to control the reaction in chemical hydrolysis.

High yields of dissolved organic substances can be obtained from both raw sludge and digested sludge. The use of pre-precipitated primary sludge is advantageous, since this has the highest COD content. Pre-precipitated primary sludge can consequently be a valuable financial asset.

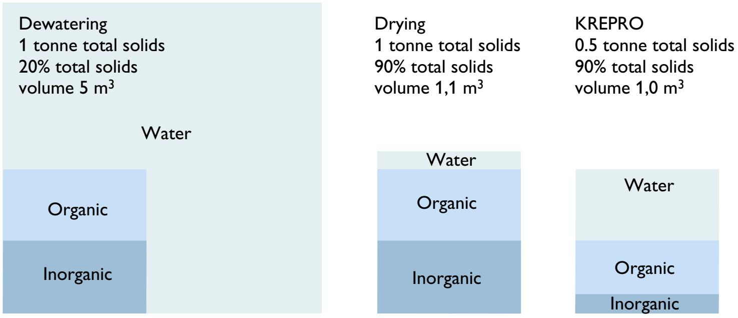
Thermal acid sludge hydrolysis

A chemical/thermal process such as the **KREPRO** process (Kemwater Recycling Process) separates wastewater sludge into four recyclable products:

- **biofuel**
- **phosphate**
- **coagulant**
- **carbon source**

Both raw sludge and digested sludge can be processed. The process is continuous. The sludge is acidified to a pH of between 1 and 3, and processed for around 60 minutes at 140°C, which brings around 60% of the suspended solids into solution.

The residue, mainly fibre, can be dewatered very easily. A total solids content of 50% is achieved by centrifuging. The volume reduction compared with conventional dewatering is around 75%. The ash content is also reduced by up to 75%.



➤ **Figure 4:3** Water, organic and inorganic fractions from different sludge processing methods.

The calorific value of the fibre fraction is high, around 8 MJ per kilo of dewatered sludge (50% DS) or about the same as wood chips. This fraction can be used for energy production by combustion. Alternatively, the composted material can be used as a mulch or for making soil. If the fibre fraction is burned, the KREPRO process can be adapted so that the heavy metals are separated with this fraction. The heavy metals can then be separated from the ash and during flue gas cleaning, then disposed of appropriately. If the fibre fraction is composted or used to make soil, the KREPRO process is adapted so that most of the heavy metals are separated during a later stage.

The reject water that is obtained during separation of the fibre fraction contains phosphorus, nitrogen, dissolved organic matter, coagulants, and unless they have been removed earlier, heavy metals. The phosphorus that is precipitated out and separated is free from heavy metals and organic environmental toxins.

The heavy metals can now be removed if this has not already been done. The reject water contains an energy-rich organic fraction that can be used for nitrogen reduction, and coagulant, which can be recycled for phosphorus reduction at the wastewater treatment plant.

Thanks to the use of heat exchangers and the high energy content of the recovered components the KREPRO process has a net energy gain.

Phosphorus fraction from KREPRO

Cleanliness

The value of sludge from treatment plants as a soil improver has been the subject of much debate. One tonne of dry matter from sludge contains around 30 kg of phosphorus, which is worth more than the cost of the coagulant that was required to obtain it. The problem is that during its passage through the wastewater system the phosphorus has become contaminated with substances that should be kept away from agricultural land and food production in a sustainable society. These substances mostly end up in the sludge with the phosphorus. It is mainly metals, organic toxins and infectious matter that enter the phosphorus cycle through the wastewater system.

The KREPRO process removes all the above-mentioned substances from the phosphorus, and results in a degree of purity that is fully comparable with the cleanest commercial fertiliser on the market. Infectious matter in the sludge is destroyed effectively during thermal hydrolysis. The process is then controlled by means of pH adjustments, so that heavy metals and organic toxins are separated with the biofuel fraction for example. What is left is a solution that is very clean in terms of the substances that contaminated the phosphorus on its way from the fields. This solution is then precipitated to give amorphous (non-crystalline) iron phosphate, which is separated and dried.

The KREPRO process produces a pure phosphorus fraction.

➤ **Table 4:9** Heavy metal content of digester sludge, KREPRO iron phosphate and P20 commercial fertiliser from Hydro.

Substance	Digester sludge (mg/kg P)	KREPRO iron phosphate (mg/kg P)	Commercial fertiliser P20 from Hydro (mg/kg P)
Cadmium	30–100	<5	37
Mercury	30–100	<0,5	0,5
Lead	1.980	100	100
Chrome	825	170	784
Nickel	825	125	130
Copper	21.450	50	135
Zinc	19.800	850	1200

➤ **Table 4:10** Organic toxins.

PCB = Poly Chlorinated Biphenyls

PAH = Poly Aromatic Hydrocarbons

PBDE = Poly Brominated Diphenyl Ethers

Substance	Digester sludge (mg/kg P)	KREPRO iron phosphate (mg/kg P)	Treatment efficiency (%)
PCB	5	<0,1	>98
PAH	50	<3	>94
Toluene	1.000	<10	>99
Nonylphenol	2.300	3,1	99,9
Dioxins	$1,6 \cdot 10^{-4}$	$4,6 \cdot 10^{-6}$	97,2
PBDE	16,7	0,36	98
Dioxin	$1,6 \cdot 10^{-4}$	$4,6 \cdot 10^{-6}$	97,2
PBDE	16,7	0,36	98

➤ **Table 4:11** Infectious matter – investigation results from SVA (National Veterinary Institute of Sweden).

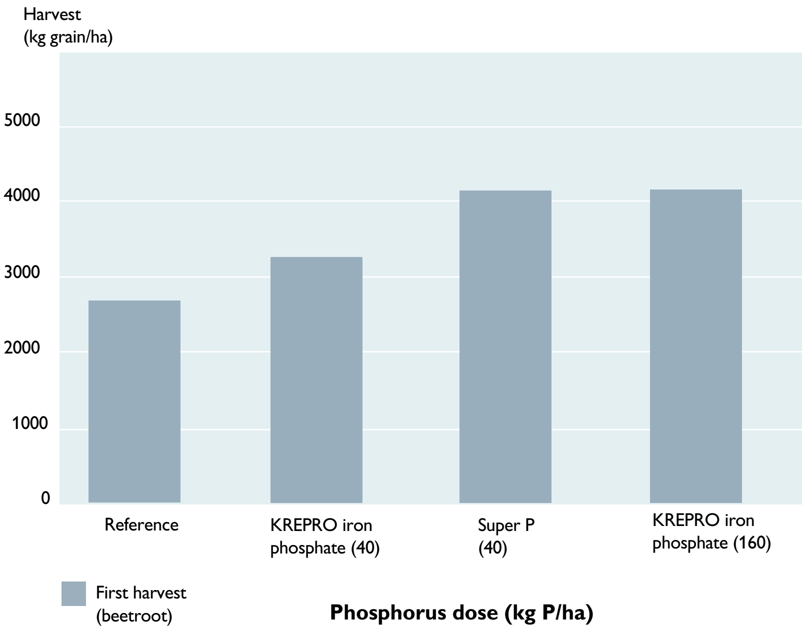
cfu = Colony forming unit/gram

	Clostridium (cfu/g)	Bacillus species (cfu/g)
Digester sludge	130.000	Overgrowth
KREPRO iron phosphate	<10	<100

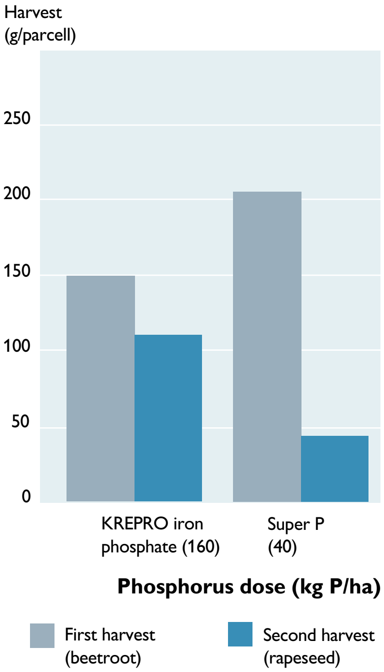
Accessibility

When a plant takes up phosphorus, complex chemical reactions take place in and around the plant's roots. These reactions are intended to separate the phosphorus from the soil and allow it to be absorbed by the plant. Modern commercial fertilisers are tailored to facilitate these reactions for different plants in different types of soil. Farm manure also contains phosphorus that is easily accessible for many plants.

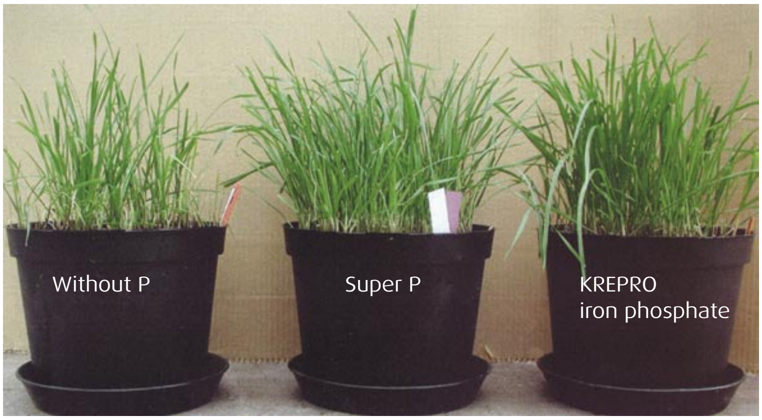
The fact that phosphorus from KREPRO is very pure does not guarantee that it is accessible to plants and hence an effective fertiliser. A number of cultivation trials have therefore been carried out in an attempt to show that phosphorus from KREPRO is accessible to different plants in different types of soil. Most of the trials gave identical results. Shown below are the results of two trials with grain, beetroot and rapeseed in soil that is low in phosphorus. The first trial with a grain crop shows that phosphorus from KREPRO has a clear effect, even though it is slightly less effective than conventional phosphorus fertiliser. In the second trial, with rapeseed and beetroot, the soil was first fertilised with phosphorus. It was then sown with beetroot, which was harvested, and then sown with rapeseed, which was also harvested without adding more phosphorus. Just as with the grain, the beetroot harvest (the first harvest) was larger when phosphorus was added in the form of conventional fertiliser. However, the rapeseed harvest (the second harvest after fertilisation) was much larger when phosphorus from KREPRO was used.



➤ **Figure 4:4** First harvest of grain with stated phosphorus dose.



➤ **Figure 4:5** Two harvests from same phosphorus dose.



➤ **Figure 4:6** Rye grass in lime-poor soil with pH 5,5 in Sahapelto, Finland.

Grass shows similar results, as do rapeseed, beetroot and birch.

Availability

Without phosphorus, biological life on this planet would not exist. It is essential for building genes and for transporting energy in all living organisms, and is present in DNA, teeth, bones and in cell membranes. Phosphorus cannot be replaced by any other element.

Phosphorus, nitrogen and potassium are the most important nutrients for plants. Calcium and sulphur are also important for the vast majority of plants, and hence for the global food supply. If the availability of any one of these substances was restricted it would mean that considerably less food could be produced at current costs. The substance that is most likely to become scarce first is phosphorus.

An element such as phosphorus cannot disappear, but it can be contaminated and spread in an uncontrolled manner that could make it a scarce resource in the future, particularly in pure form. This will naturally not happen in the next few years, but it is important to have solutions in advance, and the phosphorus issue has caused a considerable degree of concern, for a variety of reasons. Many people are debating the problem, and the solution that most favour is recycling. The fact is that phosphorus follows a fairly well known path, and a large proportion of the phosphorus used by society ends up in wastewater sludge. The ability to recover phosphorus from wastewater sludge has therefore been the goal of many research and development efforts in recent years.

Chapter 5

Costs

Chapter 5 Costs

Costs

The choice of process clearly has a big influence on the operating economics of different treatment processes. The investment cost (per volume), energy consumption, chemical precipitants and costs of sludge processing all affect operating economy.

“Wealth is like sea water;
the more we drink,
the thirstier we become.”

Arthur Schopenhauer

What does it cost to produce potable water?

In order for potable water of satisfactory quality to be supplied to consumers the water must be put through a variety of processes. These treatment methods are described in chapter 2. Good quality raw water naturally requires less treatment than water of poorer quality.

The cost of coagulants for a chemical precipitation process represents a relatively small proportion of the overall water and sewage charge.

The example below illustrates the costs of producing potable water using Kemwater ALG (aluminium sulphate) at a waterworks in a large Swedish municipality. The water and sewage charge, which covers the treatment of potable water and wastewater, amounts to € 1,25/m^3. The production of potable water accounts for the smaller share of this total, around 36% (€ 0,45/m^3).

➤ **Table 5:1** Production cost for potable water.

Costs in SEK/m^3	
Production (excl. chemicals)	0,41
Distribution	3,73
ALG, aluminium sulphate	0,053
Cost of other chemicals	0,021
Total cost	4,21

The prices in the table are from the mid-nineties.

Chemical precipitants account for just 1% of the total cost of producing and distributing potable water.

What does it cost to treat wastewater?

It is impossible to make a general assessment of costs. Local circumstances mean that the composition of wastewater varies enormously. A Danish-Norwegian university study* on behalf of the World Bank is currently comparing various treatment processes to provide a basis for future investment projects. The study does not take into account biogas generation, which does however have a significant effect on overall economy.

Assumptions

Calculations are based on 100 000 person equivalents (pe).

Flow:	**400 l/pe/d**
Load BOD:	**70 g/pe/d**
SS:	**100 g SS/pe/d**
P_{tot}:	**2,25 g/pe/d**
N_{tot}:	**12 g/pe/d**

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* Henze, M. and Ødegaard, H. (1994) An analysis of wastewater treatment strategies for Eastern and Central Europe. Wat. Sci. Tech. Vol 30, No. 5, pp 25–40.

➤ **Table 5:2** Comparison between different wastewater treatment processes.

Treatment process	Efficiency (%)			Sludge production (g SS/m^3)		
	BOD	SS	P_{tot}	N_{tot}	Before digestion	After digestion
Direct precipitation	75	90	90	10	280	176
Biological treatment	90	90	30	10	200	100
Simultaneous precipitation	90	90	85	10	240	140
Pre-precipitation	90	90	90	15	270	160
Simultaneous precipitation pre-denitrification	95	90	90	70	220	130
Biofilm pre-precipitation post-denitrification with external carbon source	95	90	90	85	32	170

In this cost comparison the overall cost of the various treatment processes is broken down into capital (with 20 year write-off at 7% interest) and operating costs. The costs of water treatment and sludge treatment are also given separately.

The sludge treatment is based on anaerobic digestion and dewatering. Biogas production has been ignored.

The overall cost for direct chemical precipitation is set at 100 and the other figures are given in relation to this. (Example: the overall cost of biological treatment is 109, i.e. 9% more expensive.)

➤ **Table 5:3** Relative costs of different treatment processes.

Treatment process	Capital	Operation	Total
Direct precipitation			
Wastewater	39	35	74
Sludge	13	13	26
Total	52	48	100
Biological treatment			
Wastewater	54	35	89
Sludge	10	10	20
Total	64	45	109
Simultaneous precipitation			
Wastewater	56	46	102
Sludge	12	11	23
Total	68	57	125
Pre-precipitation			
Wastewater	50	42	92
Sludge	15	14	29
Total	65	56	121
Simultaneous precipitation and pre-denitrification			
Wastewater	85	67	152
Sludge	12	12	24
Total	97	79	176
Biofilm pre-precipitation – post-denitrification with external carbon source			
Wastewater	67	73	140
Sludge	15	14	29
Total	82	87	169

For comparable processes, chemical pre-treatment of wastewater has a beneficial effect on the overall operating economy.

6

Chapter

Environmental impact

Chapter 6 Environmental impact

Environmental impact

Everything in our daily lives – the food we eat, the newspapers we read, the lights we use, the water we drink, and so on – affects the environment in some way.

The total environmental impact of our various activities has caused growing concern in recent years. In order to reduce the environmental impact of a given activity or product every stage of its life must be taken into account and analysed. In other words its environmental impact must be considered "from cradle to grave".

In order to identify and document environmental damage a variety of tools known as life cycle analyses (LCA) have been developed. These life cycle analyses can naturally also be used in the water treatment field to identify the products, processes and activities that have the least possible environmental impact.

"The great rivers
need the small streams."

Albert Schweitzer

What is a life cycle analysis?

A life cycle analysis is a structured method that is used to assess a product, service or activity and its environmental impact. During the analysis a comparison is always to be made with a similar product or activity. The goal is to compare different activities that give the same results.

For example, one could ask the question whether it is better to use disposable cups for drinking coffee, or to use china mugs that can be washed and reused.

Wastewater treatment processes can be analysed in a similar way.

In a life cycle analysis each type of impact is classified according to the effect it has on nature. Some forms of impact can be put into more than one class. This quantitative assessment is often inadequate and we therefore also need a more qualitative method to assess the overall impact within each class. By applying various weighting factors we can obtain an overall result that reflects the relative significance of each effect.

A comparison is made between two or more products or processes that give similar performance. All components are considered in the analysis, together with raw materials, energy consumption, transport and processes. The emissions that result from each stage are added together and their environmental impact is evaluated.

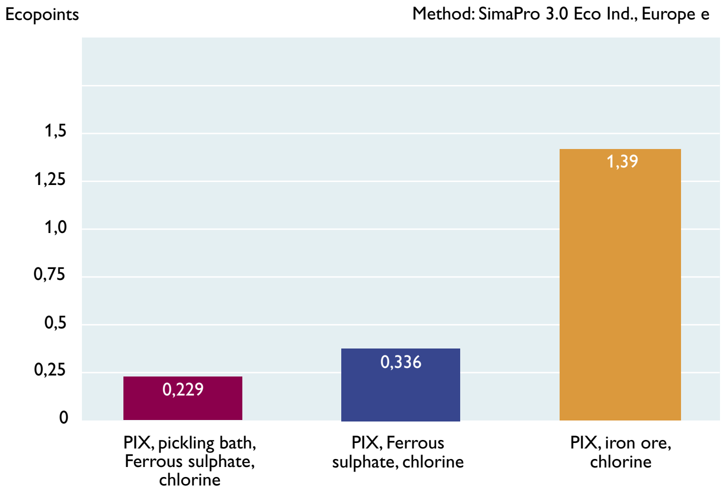
If a given activity has a low impact in every class then the results are easy to interpret. This is not always the case, but the results can still be added together to give a final score that is measured in "ecopoints".

So what happens if the eutrophication arising from a given activity, in this case a wastewater treatment process, has a high impact, but the process has a low impact in all other respects? What is the best choice in environmental terms? There are simulation programs that weigh the various factors into the assessment and add the scores in each class to give an overall result.

Simulation

In the examples a program SimaPro was used to do the life cycle analyses. SimaPro evaluates 11 different environmental parameters to give an impact score in ecopoints. The higher the score in ecopoints, the greater the negative impact a parameter has on the environment. A life cycle analysis can never be comprehensive and always entails some simplification, but it is currently the best method for evaluating environmental impact.

Simulations carried out using SimaPro can, for example, be used to identify the raw materials and manufacturing processes that have the least environmental impact when making coagulants. A variety of raw materials can be used for the manufacture of Kemwater PIX, for example, such as iron ore, iron sulphate, pickling baths, hydrochloric acid, sulphuric acid, and oxidants such as chlorine.



➤ **Figure 6:1** Ecopoint scores for the manufacture of trivalent iron salts using various raw materials.

It is clear that recycled materials, such as pickling baths and iron sulphate, are less harmful to the environment than raw materials that are extracted straight from the earth's crust as iron ore. Techniques now exist for processing and treating industrial by-products that contain aluminium or iron. These techniques allow a large proportion of a waste product, which would otherwise be dumped as landfill, to be recycled and serve a useful purpose.

Another important parameter in a life cycle analysis is energy consumption. The following amounts of energy are used to produce 1 tonne of coagulant.

➤ **Table 6:1** Energy consumption for production of 1 tonne of coagulant.

		kWh	
	PIX	**AVR**	**PAX**
Raw material	50–100	200	150
Production	40	50	100
Transport	60	70	60
Total	**200**	**320**	**310**

It is possible to compare chemical and biological treatment in terms of energy efficency. This means that during direct precipitation, 1 kWh of energy is required to remove 5 kg of BOD. In biological treatment 1 kWh of energy removes just 1 kg of BOD.

It is also possible to compare wastewater treatment processes by using an LCA. Energy consumption plays a major part in such a comparison. Three pairs of comparable processes are presented in figure 6:2 and compared in table 6:2.

- **high-load activated sludge process with direct precipitation**
- **simultaneous precipitation with pre-precipitation**
- **biological phosphorus and nitrogen reduction using pre-precipitation and biological nitrogen reduction with an external source of carbon**

➤ **Table 6:2** Supplied and recovered energy and the transport of sludge.

			kWh per day		
	Coagulants	**Active sludge**	**Biogas**	**Sludge transport**	**Energy balance**
Activated sludge process	0	8 000	7 800	300	-500
Direct precipitation	1 600	0	9 000	400	+7 000
Simultaneous precipitation	800	5 600	7 800	310	-1 090
Pre-precipitation	1 200	2 800	9 900	410	+5 490
Biol. P and N reduction	0	8 000	7 800	310	-510
Pre-precipitation, N reduction HYPRO	960	6 000	10 600	420	+3 220

The assumptions made in the comparison shown in table 6:2 are:

- It takes 1 kWh of energy to remove a 1 kg load of BOD in an activated sludge process.

- The oxidation of 1 kg of ammonia into nitrate requires 5 kWh.

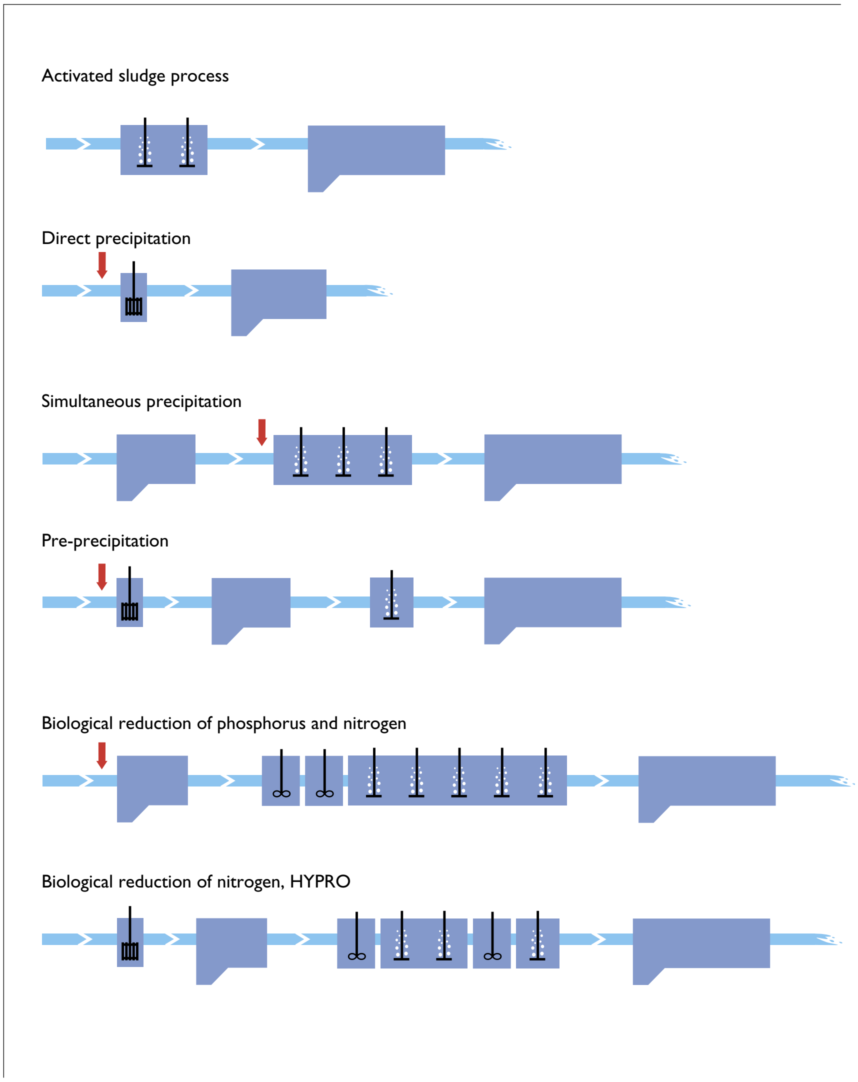
- It takes 200 kWh of energy to produce and transport 1 tonne of coagulant (Kemwater PIX).

- Dosage: direct precipitation 200 g/m^3; simultaneous precipitation 100 g/m^3; pre-precipitation 150 g/m^3; biological P and N reduction, no coagulant; pre-precipitation with N reduction, HYPRO 120 g/m^3.

- Energy from biogas: 1 kg BOD yields 1,5 kWh of electricity, but is not included in the LCA analysis.

- The lifetime of the treatment plant is 30 years.

All figures used in the study are calculated per day (concrete, transport, energy, coagulants etc.).



➤ **Figure 6:2** The treatment processes that were used in the example calculation in table 6:2.

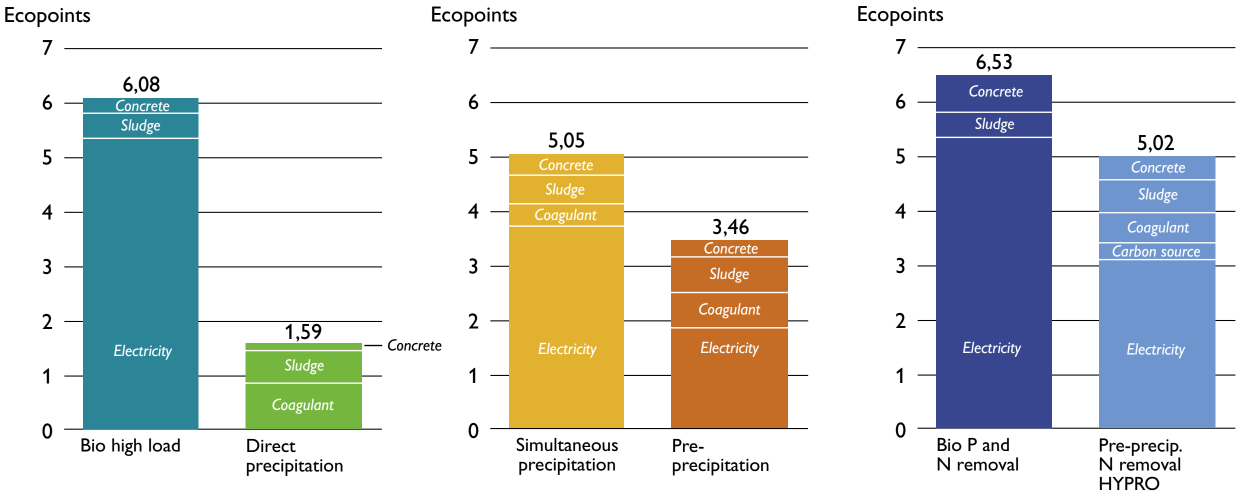
Wastewater treatment

Wastewater treatment protects the recipient water from organic matter, nutrients, bacteria and viruses. The efficiency of treatment can be described in terms of primary and secondary oxygen demand. The primary oxygen demand refers to the breakdown of biological matter (BOD) and the oxidation of ammonia to nitrate.

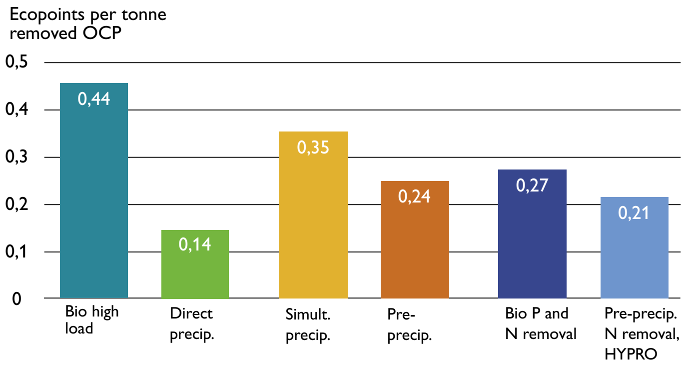
Secondary oxygen demand is caused by the breakdown of the algae that are formed due to the availability of phosphorus and nitrogen.

The reduction of primary and secondary oxygen consumption potential (OCP) for different recipients can be estimated in order to compare the efficiency of different treatment processes.

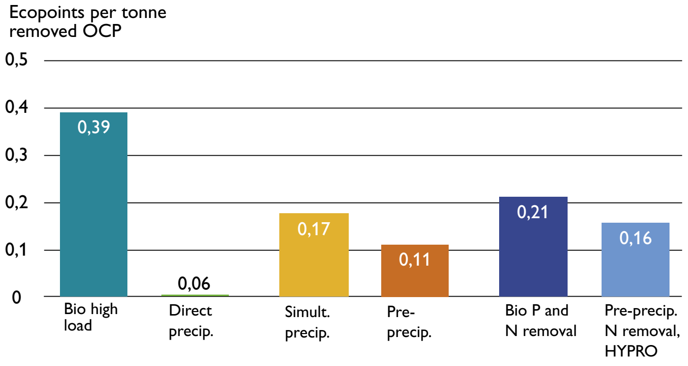
Two types of recipients are assumed: one in which nitrogen is the limiting growth factor, and another in which phosphorus is the limiting growth factor. The environmental efficiency expressed as the reduction in OCP units per ecopoint makes it possible to compare all processes for the same type of recipient.



➤ **Figure 6:3** Ecopoints for different processes.



➤ **Figure 6:4** Ecopoints for different treatment processes where nitrogen is the limiting factor for eutrophication of the recipient.



➤ **Figure 6:5** Ecopoints for different treatment processes where phosphorus is the limiting factor for eutrophication of the recipient.

Conclusion

Processes that are based on direct precipitation or pre-precipitation are very competitive when compared with biological processes in terms of total environmental impact.

Chapter 7

Precipitation & Flocculation

Chapter 7 Precipitation & Flocculation

Precipitation & Flocculation

Around two-thirds of the Earth's surface is covered by water. 98% of all the water on the Earth is saltwater. The remaining 2% is sweet water or fresh water. Of the total amount of fresh water, 80% is bound as ice in cold regions, and of the remaining 20%, the majority, 99%, is present as ground water and 1% as rivers and lakes.

Groundwater can easily be converted into drinking water without especially extensive treatment. Occasionally soluble Fe^{2+} and sometimes Mn^{2+} have to be oxidised into their solid forms, which are then removed. The oxidation is often done by air, although chemicals are sometimes used, especially for oxidising Mn^{2+}.

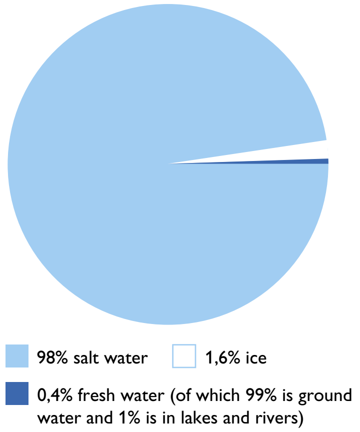
All water that is intended for consumption, whether it derives from groundwater or surface water, is disinfected in order to kill pathogens (microorganisms that spread disease) before it is distributed to users.

Surface water is often coloured and contains different types of particles, e.g. bacteria, viruses, parasite eggs, organic decomposition products and waste products. These substances should be removed before the water is disinfected.

When the water closet began to be more widely used at the start of the twentieth century the authorities were initially reluctant to permit its widespread use. It was feared that the recipient water would become infected. However, public pressure grew strong and the authorities began granting more and more permits.

"He who neglects to drink at the spring of experience is likely to die of thirst in the desert of ignorance."

Ling Po



➤ **Figure 7:1** The Earth's water resources.

Nowadays, water closets are widely used all over the world. Before wastewater is led into the recipient water it must first be treated. If the wastewater is led into a river or lake its phosphorus content should be reduced. If it is led into salt water its nitrogen content should be reduced. In both cases it is important to remove oxygen-depleting substances.

If this is not done the recipient water will suffer eutrophication, i.e. algae and other microorganisms will begin to grow there and at times will cover its surface like a green blanket. At such times these microorganisms can release substances that are toxic to people and animals. We must therefore treat wastewater before it is released into a waterway.

This chapter describes how different chemicals can be used to treat both surface water and wastewater.

Different types of contaminants in water

Contaminants in water can either take the form of particles, or be so small that they are soluble.

Dissolved substances in wastewater can include sugars or orthophosphates, while soft surface water can contain fulvic and humic acids that colour the water.

Table 7:1 shows the distribution of TOC, COD, proteins, fat and carbohydrates in wastewater in terms of particle size.

➤ **Table 7:1** How the content of COD, TOC, fat, protein and carbohydrate is distributed in soluble and particle form in wastewater. The figures in brackets are taken from the middle reference.

Parameter	Soluble <0,08 µm	Colloidal particles 0,08-1,0 µm	Supercolloidal particles 1-100 µm	Sedimenting particles >100 µm
% total COD	25 (40)	15 (10)	26 (21)	34 (29)
% total TOC	31 (42)	14 (11)	24 (20)	31 (27)
% total fat	12	51	24	19
% total protein	4	25	45	25
% total carbohydrates	58	7	11	24
Biochemical oxidation rate	0,39	0,22	0,09	0,08

(References: Heukelekian, H. and Balmat, J.L., Chemical Composition of the Particulate Fraction of Domestic Sewage, Sewage and Industrial Wastes, 31(5), 1959:4, 413–423; Rickert, D.A. and Hunter, J.V., General Nature of Soluble and Particulate Organics in Sewage and Secondary Effluent, Water Research 5, 1971, 421–436; Balmat, J.L., Biochemical Oxidation of Various Particulate Fractions of Sewage, Sewage and Industrial Wastes, 1957, 29(7), 757–761.)

The table shows that most of the contaminants in wastewater are in the form of particles.

The significance of particle size in sedimentation

The time needed for a particle to sediment depends on its density and size.

Sand and clay often have a density of around 2,65 g/cm^3.

The density of flocs depends on their size and the amount of coagulant used. The floc density decreases with increasing floc size and is often around 1,02 till 1,1 g/cm^3.

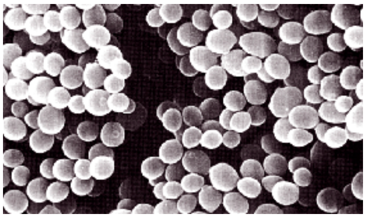
Table 7:2 shows how long it takes spherical particles of different diameters to settle 1 metre in stationary water if they have a density of 1,05, 1,10 and 2,65 g/cm^3 respectively, provided that their sedimentation behaviour follows Stokes' law.

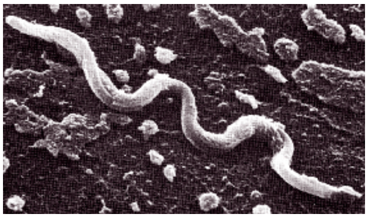
Flocs do not have a spherical form and their settling behaviour therefore does not obey Stokes' law. However, the table does give a useful guide to the time required for sedimentation.

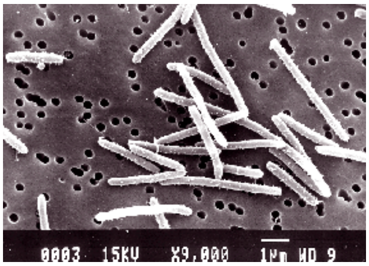
➤ **Table 7:2** Influence of particle diameter on the time required for particles to settle 1 m in stationary water at a temperature of 25°C, assuming that particle sedimentation follows Stokes' law and that particles have a density of 1,05, 1,10 and 2,65 g/cm^3 respectively. The table also shows the surface area of 1 cm^3 of particles of different sizes.

Particle diameter	Sedimentation time (1,05 g/cm^3)	Sedimentation time (1,10 g/cm^3)	Sedimentation time (2,65 g/cm^3)	Total particle area (m^2/cm^3)
1 mm	37 seconds	18 seconds	1 second	0,006
0,1 mm	1 hour	31 minutes	2 minutes	0,06
10 µm	4 days	2 days	3 hours	0,6
1 µm	1 year	0,6 year	13 days	6
0,1 µm	117 years	58 years	3,5 years	60

It can be seen from table 7:2 that particles with a size of 1 mm or larger settle out quickly. Particles of colloidal size are, however, impossible to sediment without using centrifuges or by aggregating them into larger units.


➤ **Figure 7:2a** Bacteria with a spherical form (Staphylococcus aureus).


➤ **Figure 7:2b** Spiral-shaped bacterium (Cristispira).



➤ **Figure 7:2c** Rod-shaped bacteria.

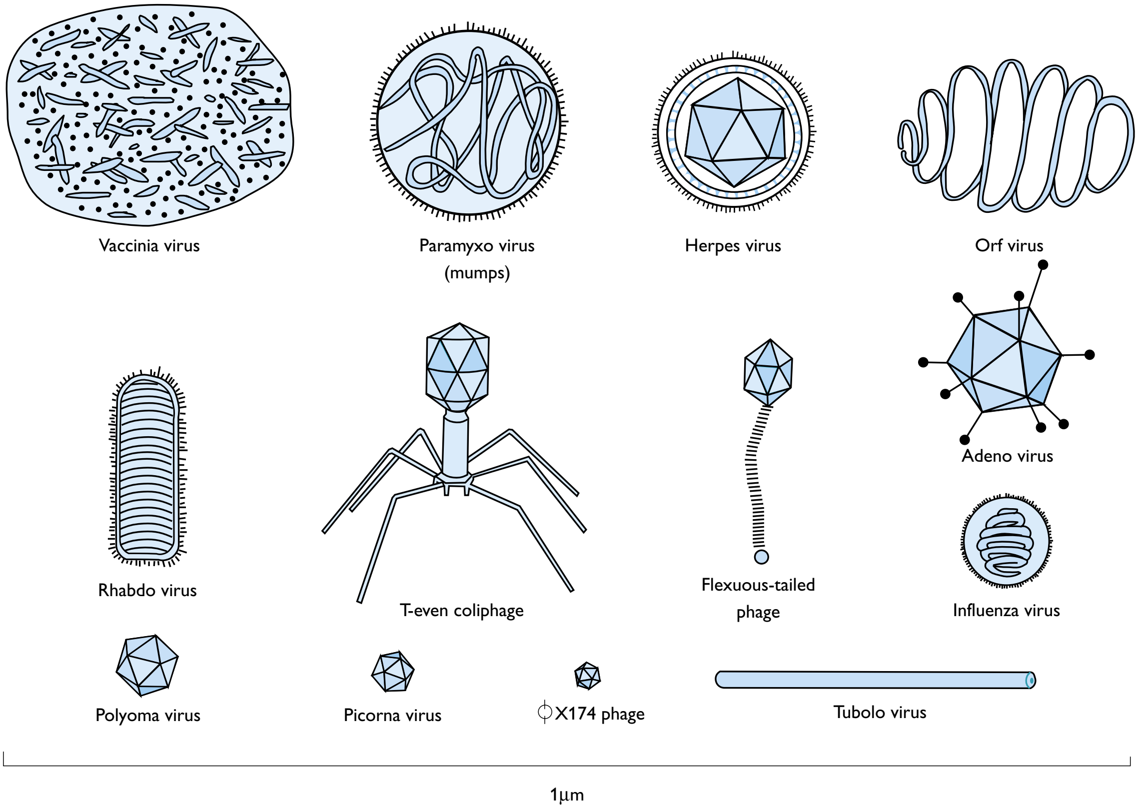
With decreasing water temperatures the sedimentation time increases (mainly due to the increasing viscosity of water). At 5°C about 50% higher sedimentation times are needed as compared to the times given in the table above.

The smaller the particle is, the larger its relative surface area. Surface forces between small particles play a decisive role in their tendency to aggregate.

The smallest particles visible to the naked eye have a diameter of about 40 µm. Particles with smaller diameters are perceived as turbidity. Particles with a size similar to the wavelength of light, i.e. 0,4–0,7 µm, make a large contribution to turbidity. The more the particle size deviates from the wavelength of light, the less turbidity they will cause.

Bacteria are either spherical or rod-shaped particles often with sizes varying between 0,35 and 35 µm. See figures 7:2a–c.

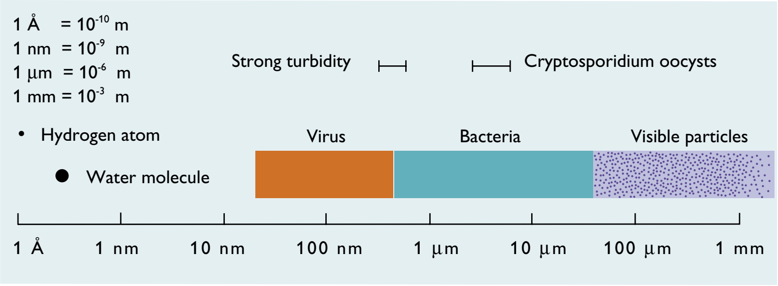
Viruses are very small particles with sizes of about 0,02–0,4 µm.



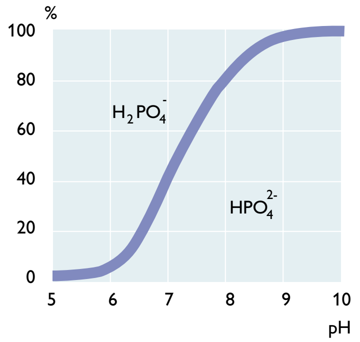
➤ **Figure 7:3** Different types of virus.

Particles that are so small that they do not sediment naturally are called colloidal particles.

They are said to be stable if they do not aggregate, and unstable if they aggregate readily.



➤ **Figure 7:4** Logarithmic size range.



➤ **Figure 7:5** The influence of pH on the relative distribution of dissolved orthophosphate with one and two minus charges respectively.

Different phosphorus contaminants in wastewater

Of the total phosphorus content in wastewater, the bulk, 50–80%, is present as soluble orthophosphate.

In wastewater, orthophosphate exists either in the form of $H_2PO_4^-$ or as HPO_4^{2-}. The relative amounts of these two forms depend on the pH (see figure 7:5).

Some detergents contain tripolyphosphates, which are gradually converted to orthophosphate in the wastewater system. If the distance between households and the wastewater treatment plant is short, the wastewater may contain triphosphates. Both orthophosphates and polyphosphates can be precipitated with the aid of aluminium and iron salts.

The second most common form of phosphorus in wastewater is as particles.

All bacteria contain nucleic acids, which are rich in phosphorus. Besides this phosphorus, bacteria also have a layer of phospholipids in their cell membranes.

Viruses, which are also particles, contain a lot of phosphorus. They have a core of nucleic acids surrounded by a protein layer.

Particles can be precipitated with the aid of aluminium and iron salts.

Finally, wastewater contains small amounts of certain phosphorus compounds, e.g. AMP, ADP, ATP (adenosine monophosphates, diphosphates and triphosphates respectively), free phospholipids, lecithin etc.

Contaminants that can be removed by chemical treatment

From table 7:1 on page 157 it can be seen that the largest proportion of the contaminants in wastewater are present as particles.

Removal of particles

Surface water contains a variety of particles, such as insect eggs, bacteria, viruses, waste and debris products, clay, sand, etc. Many of them present a health hazard, and their presence increases the amount of disinfectant needed before water can be distributed to consumers. High concentrations of disinfectant can give water an unpleasant taste. Some parasite oocysts, e.g. Cryptosporidium, which have a spherical shape and a diameter of about 3–7 µm, do not seem to be killed by the most common disinfectants. In order to eliminate the risk of epidemics it is therefore important to remove them before distributing the water.

Other particles that must be removed or killed include Giardia, which has an oval to spherical shape and measures 5–15 x 8–18 µm, Legionella, Cholera, and pathogenic viruses.

Aluminium and iron salts have the ability to aggregate particles into such sizes that they can be removed.

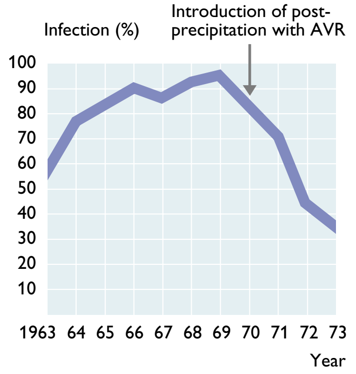
The reason for this is that almost all particles in natural water are charged. Most of them have a net negative charge. They therefore repel each other and remain dispersed in the liquid if they cannot find something to adsorb to.

Aluminium and iron ions are positively charged. They form polymer ions and hydroxides that bind to small particles and create flocs, which can be separated from the water relatively easily.

The use of chemicals for water treatment in recent decades has improved our environment.

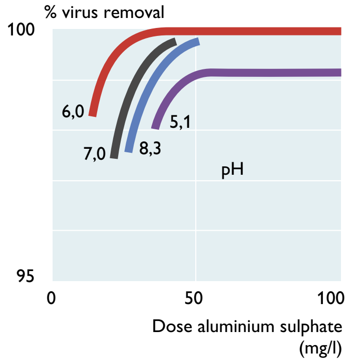
Figure 7:6 shows how the introduction of chemical treatment with an aluminium salt at a popular bathing lake in the south of Sweden reduced the number of tapeworm eggs in the lake. The tapeworm eggs infected fish, which in turn infected people if eaten without having been properly cooked.

Figure 7:7 shows that viruses, which are very small particles, can be extensively removed by chemical treatment.



➤ **Figure 7:6** % tapeworm infection during different years in the lake Ivösjön in Sweden. Chemical treatment was introduced 1970.

(Reference: Almer, B. Bekämpning av binnikemasken, Biphyllobothrium latum. Information från sötvattenslaboratoriet, nr. 15 (1973), Sweden.)



➤ **Figure 7:7** The influence of pH and the dose of aluminium sulphate on the % virus removal.

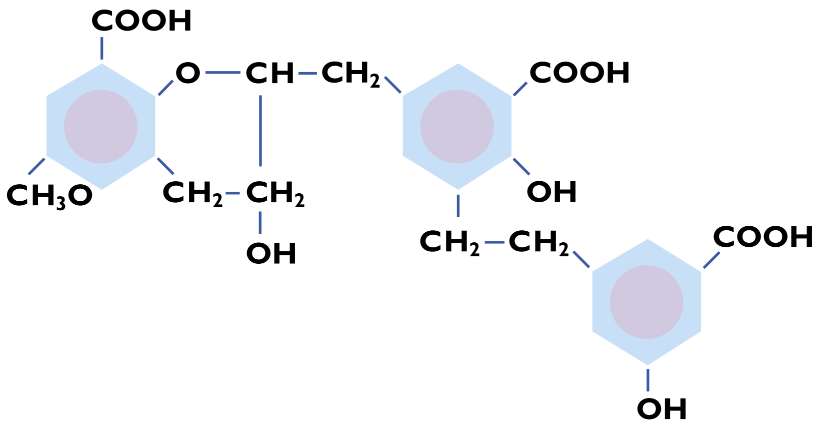
(Reference: Chadhur M and Engelbrecht R. Removal of viruses from water by chemical coagulation and flocculation. JAWWA (1970) 31.)

Removal of dissolved substances

Most dissolved contaminants with a negative charge can be precipitated and removed by chemical treatment.

Soft surface water often has a yellowish or brownish colour that comes from fulvic and humic acids. These are formed when trees, bushes and leaves decompose. They are aromatic and contain carboxylic, phenolic, ketone and methoxy groups. Humic acids have a higher molecular weight (1000–10000) than fulvic acids (500–2000). Both types of compound can be precipitated and removed by metal salts.

Various metal ions can also be bound to the hydroxides formed by the added aluminium or iron salt. More can be read about this effect on page 188.



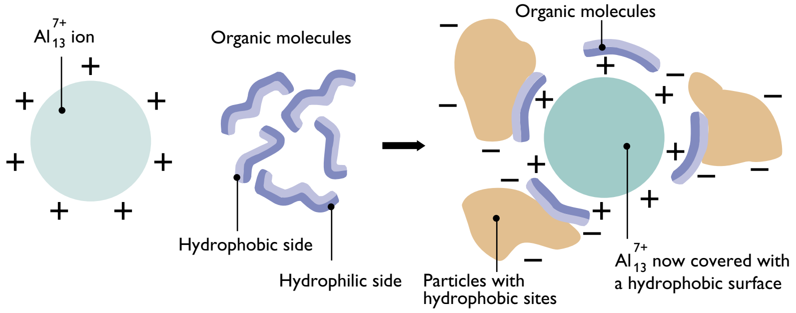
➤ **Figure 7:8** Possible structure of a fulvic acid.

In wastewater, orthophosphate and triphosphate are examples of dissolved substances that can be removed by adding metal salts. In wastewater there are also many particles that contain phosphorus, which can be removed by chemical treatment.

Most substances that have a low molecular weight and no charge, such as carbohydrates, are not removed by chemical precipitation. These low molecular weight substances can be removed efficiently by biological processes.

Aluminium and polyaluminium compounds, however, have the ability to form strong complexes with a number of uncharged, low molecular weight organic compounds, such as maltol.

These organic substances bind to the aluminium or polyaluminium ions in such a way that the hydrophilic (water-loving) end of the organic molecule points towards the surface of the aluminium compound, while its hydrophobic (water-repellent or fat-loving) end points towards the aqueous phase. In this way, part of the surface of the aluminium compound becomes hydrophobic and can cross-link and precipitate particles that have hydrophobic sites. Some microorganisms have surfaces that are covered with hydrophilic polymers. It is known that when aluminium ions bind to some of these polymers the polymer layer becomes hydrophobic. When this happens the microorganisms aggregate through hydrophobic interaction and precipitate out.
(Reference: Carel J. van Oss, Interfacial Forces in Aqueous Media, Marcel Dekker, Inc. 1994.)

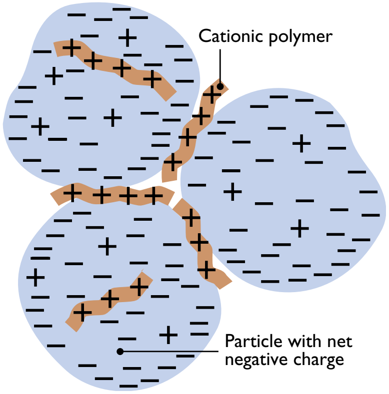


➤ **Figure 7:9** Illustration of how an uncharged organic molecule can bind to a polyaluminium ion and impart hydrophobic properties to the polyaluminium ion, and thereby enhance its tendency to bind to and precipitate hydrophobic material.

How easily are contaminants removed?

The higher the molecular weight of a dissolved substance or the larger a particle is, the easier it is to precipitate it out.

The precipitation of particles and dissolved substances is governed by different chemical rules. There are many different chemicals on the market with different relative abilities to precipitate particles or dissolved substances.



➤ **Figure 7:10** Precipitation of negatively charged particles by patch adsorption and cross-linking with cationic polymers (patch flocculation).

Coagulation and flocculation

Unfortunately, different authors do not use these terms consistently in the literature on water treatment.

La Mer originally defined coagulation as the process of reducing the electric repulsion between particles by the addition of simple salts. The particles then aggregate as a result of the remaining attraction forces between the particles.

He defined flocculation as the process of aggregating particles with the aid of polymers. He considered the bridging action of the polymers to be very important in flocculation.

The bridging action of polymers is important, and there are many electron microscope pictures that show that polymers form thin filaments that join different particles together.

However, we now know that polymers can also precipitate particles by means of patch adsorption and cross-linking, see figure 7:10. High basicity polyaluminium ions probably aggregate particles by means of this mechanism. For this reason it is now difficult to use these two words in the same way as La Mer did.

Some authors now define coagulation as the process whereby charged particles are neutralised, and flocculation as the process whereby the neutralised/destabilised particles join together and form aggregates.

Other authors just use the word flocculation as a generic term to cover all aggregation processes.

Reactions that occur when a solution of Al^{3+} or Fe^{3+} salts is added to water

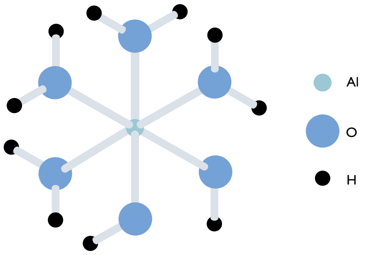
The reaction sequence below illustrates the immediate reactions that occur when a simple aluminium salt is added to water.

Corresponding reactions occur with Fe^{3+}. However, the polymerisation reactions of ferric salts differ from those of aluminium salts.

Let us first look at a concentrated solution of an aluminium salt that does not contain any counter ions bound to the aluminium ions. Aluminium chloride is one example of such a salt. In this solution, each aluminium ion is surrounded by six tightly bound water molecules.

The aluminium ions in the aqueous solution thus have the chemical formula $Al(H_2O)_6^{3+}$. Outside this ion are a further 10–12 water molecules that are bound less tightly to the $Al(H_2O)_6^{3+}$ than the inner sphere of six water molecules.

Surrounding the aqueous aluminium ions are negatively charged ions that also contain some tightly bound water molecules.



➤ **Figure 7:11** The positions of water molecules in the $Al(H_2O)_6^{3+}$ complex.

(Reference: Karlsson Magnus, Structure Studies of Aluminium (III) Complexes in Solids, in Solutions and at the Solid/Water Interface, Doctor's thesis, 1998, Umeå University, Sweden.)

Although the solution looks like ordinary water it contains very little free water with the same properties as the water you get from the tap. Almost all the water in a concentrated aluminium salt solution is tightly bound to the ions. The freezing and boiling points of the solution therefore differ from those of ordinary water.

When a concentrated solution of an aluminium or iron salt is added to water the Al^{3+} and Fe^{3+} ions react so strongly with the water that it is dissociated into hydrogen and hydroxide ions.

$$Al^{3+} + H_2O \rightarrow AlOH^{2+} + H^+$$

The above ions also contain chemically bound water molecules, but for the sake of clarity these are not shown in this or the following formulae.

The newly formed aluminium hydroxide ion reacts with water in two stages, as shown below:

$$AlOH^{2+} + H_2O \rightarrow Al(OH)_2^+ + H^+$$

$$Al(OH)_2^+ + H_2O \rightarrow Al(OH)_3 + H^+$$

Both these reactions occur very quickly.
All three reactions are completed within 1 to 7 seconds.

During the first second after the concentrated aluminium salt solution is added to the water, the aluminium ions exist mainly as Al^{3+} and $AlOH^{2+}$ and to a lesser extent as $Al(OH)_2^+$.
Suppose that one litre of wastewater contains 8 mg of P in the form of orthophos-

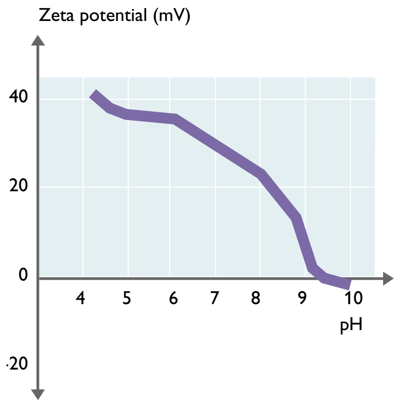
phate. This solution contains 222 222 times more water molecules than orthophosphate ions. (The wastewater contains 1000/18 moles of water and 0,008/32 moles of ortho P. It thus contains (1000/18)/(0,008/32) = 222 222 times more water molecules than ortho P ions.)

When the concentrated aluminium salt solution is added to water the likelihood that the Al^{3+} will find and react with water is much greater than the likelihood that it will react with $H_2PO_4^-$.

➤ **Figure 7:12** It is important to add the metal salt solution at a point where there is high turbulence. By doing so the ions in the metal salt solution are used more effectively.

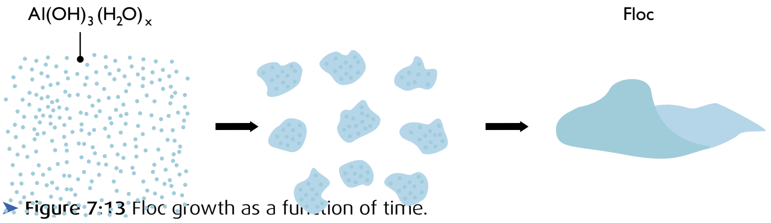
In order to increase the likelihood of the metal ions in the concentrated metal ion solution binding to the contaminants in the water that is being treated, it is important to add the coagulant somewhere where there is high turbulence. In turbulent locations the probability of Al ions quickly finding a contaminant to react with is greater than in stationary water. (Figure 7:12.)

Even with good agitation it is inevitable that $Al(OH)_3$ is formed. Initially the aluminium hydroxide is formed as small clusters with loosely bound water molecules. With time the aluminium hydroxide loses more and more water molecules. Aluminium hydroxide molecules start to aggregate by hydrogen bonding. Flocs start to form and soon become visible.



➤ **Figure 7:14** The influence of pH on the zeta potential of hydroxides produced from aluminium chloride.

Taken from Öhman L.-O. and Wågberg L., Freshly Formed Aluminum (III) Hydroxide Colloids Influence on Aging, Surface Complexation and Silicate Substitution. Pulp Paper Sci. (1997) 23(10), J475–J480.



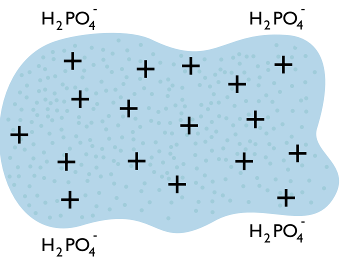
➤ **Figure 7:13** Floc growth as a function of time.

Depending on the pH, the hydroxides have a net positive or negative charge. Figure 7:14 shows the influence of pH on the charge on the hydroxides produced from aluminium chloride.

The negative ion of the salt that was used to prepare the aluminium hydroxide also influences the charge on the aluminium hydroxide.

If hydroxide is precipitated from a solution of aluminium sulphate it takes the form of aluminium sulphate hydroxide, $Al(OH)_{3-2x}(SO_4)_x$, where x is around 0,25 and the pH at which the hydroxide has zero charge is displaced about 1 pH unit towards a more acidic pH in comparison with the flocs that are formed from aluminium chloride.

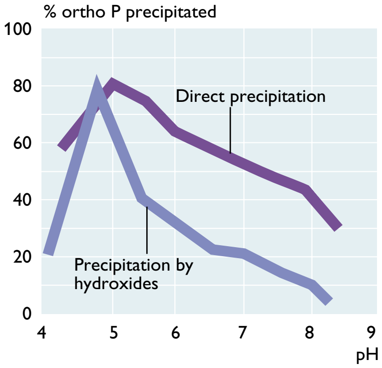
At pH levels < 9,5 the aluminium hydroxide that is produced from aluminium chloride is positively charged and can adsorb negatively charged substances, such as ortho P.



➤ **Figure 7:15** Orthophosphate ions that are adsorbed on to a positively charged aluminium hydroxide floc.

Aluminium hydroxide can therefore also be used for the adsorption of orthophosphate (figure 7:15). However it is considerably less effective at removing orthophosphate than Al^{3+} and its hydrolysis products.

Figures 7:16 and 7:17 illustrate the influence of pH when precipitating ortho P with a constant dose of aluminium and ferric sulphates respectively. Ortho P was precipitated by adding concentrated aqueous solutions of the metal salts to solutions of ortho P, and by adding solutions of ortho P to 20-minute-old metal hydroxides.
(Reference: Gillberg, L., Nilsson, D., Åkesson, M., The influence of pH when Precipitating Orthophosphate with Aluminium and Iron Salts. In: Chemical Water and Wastewater Treatment IV, Hahn, H.H., Hoffman, E., Ødegaard, H. (Eds.), Springer-Verlag, 1996, pp 95–105 (ISBN 3-540-61624.)



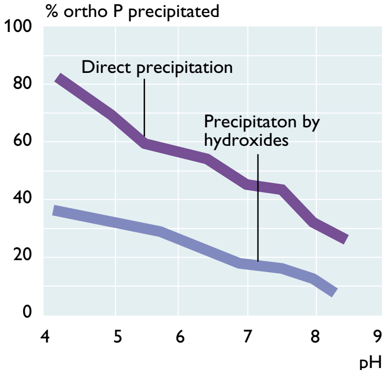
➤ **Figure 7:16** The influence of pH on the percentage of precipitated P when 0,25 mmol of Al^{3+} is added as aluminium sulphate to 0,25 mmol of ortho P (=8.0 mg ortho P/l) and after adding a solution of ortho P to the hydroxides formed from the aluminium sulphate. The solutions of ortho P were prepared in such a way that they had the same pH as the aqueous phase of the hydroxides.

From figures 7:16 and 7:17 it can be seen that considerably more ortho P was precipitated by direct addition of the salts than by the hydroxides.

The results show that it is important to ensure satisfactory mixing during the first few seconds after the salts are added to the wastewater that is being treated. The less effective the mixing, the more hydroxide will be formed, which is less effective at removing ortho P.

It is also important to ensure good mixing when adding the metal salt solution to precipitate particles.

Both aluminium and ferric ions and their hydroxides tend to polymerise.

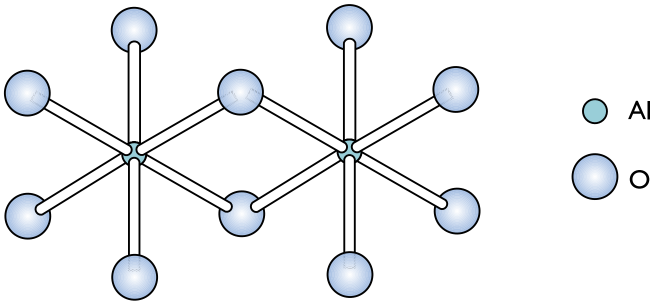


➤ **Figure 7:17** The influence of pH on the percentage of precipitated P when 0,25 mmol Fe^{3+} is added as ferric sulphate to 0,25 mmol of ortho P (=8,0 mg ortho P/l) and after adding ortho P to hydroxides formed from the ferric sulphate. The solutions of ortho P that were added to the hydroxides had the same pH as the aqueous phase of the ferric sulphate hydroxides.

The simplest ion that is formed with more than one aluminium atom is the dimeric ion (an ion with two metal atoms):

$$2Al^{3+} + 2H_2O \rightarrow Al_2(OH)_2^{4+} + 2H^+$$

$$2Al(OH)_3 \rightarrow Al_2(OH)_2^{4+} + 4OH^-$$



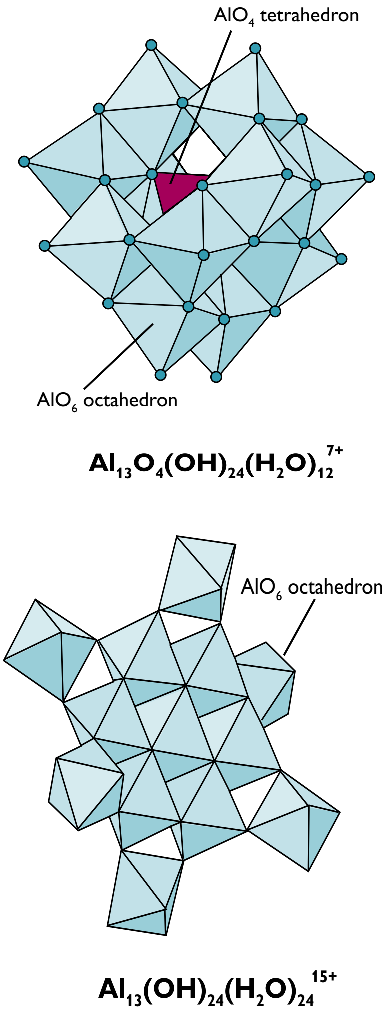
➤ **Figure 7:18** Positions of aluminium and oxygen atoms in the dimeric aluminium ion. For the sake of clarity the hydrogen atoms are not shown in the molecule.

There are many other polymeric aluminium ions. Many of them have a short lifetime and are therefore difficult to identify. However, some polymeric aluminium ions do exist, e.g. the well-known $Al_{13}O_4(OH)_{24}(H_2O)_{12}{}^{7+}$, which is relatively stable at certain pH levels.

Another polyaluminium ion with 13 aluminium atoms, having the formula $Al_{13}(OH)_{24}(H_2O)_{24}{}^{15+}$, was identified in 1998 using X-ray techniques by a research team in the north of Sweden.

(Reference: Karlsson Magnus, Structure Studies of Aluminium (III) Complexes in Solids, in Solutions and at the Solid/Water Interface, doctoral thesis, 1998, Umeå University, Sweden.)

Figure 7:19 shows the molecular structure of the two known Al_{13} ions.



$Al_{13}O_4(OH)_{24}(H_2O)_{12}{}^{7+}$

$Al_{13}(OH)_{24}(H_2O)_{24}{}^{15+}$

➤ **Figure 7:19** The molecular structure of the two known Al_{13} ions.

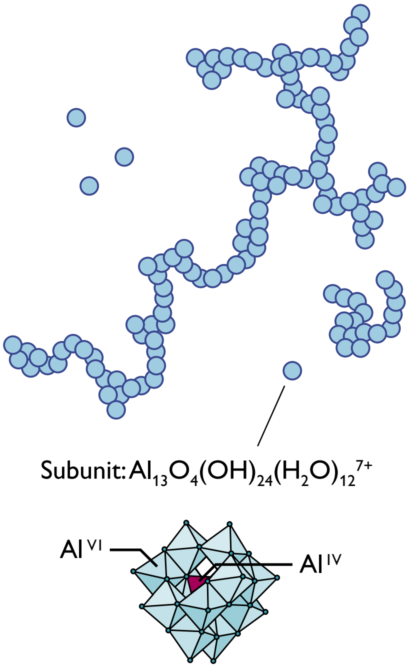
Some authors believe that at least one of the Al_{13} ions is capable of polymerisation. The imagined structure of polymerised Al_{13} ions is shown in figure 7:20.

Table 7:3 shows the composition and properties of different, well-studied aluminium ions:

➤ **Table 7:3** Basicity and other properties of some well-studied aluminium compounds.

Formula	Molar ratio OH^-/Al^{3+}	Relative basicity %	Number +charges per ion	Number +charges per Al atom and Number H^+ released when $Al(OH)_3$ is formed	Number H_2O molecules per Al atom
$Al(H_2O)_6^{3+}$	0	0	3	3	6
$Al_2(OH)_2(H_2O)_8^{4+}$	1	33	4	2	4
$Al_{13}(OH)_{24}(H_2O)_{24}^{15+}$	1,85	62	15	1,15	1,85
$Al_{13}O_4(OH)_{24}(H_2O)_{12}^{7+}$	2,46	82	7	0,54	0,92
$Al(OH)_3(H_2O)_x$	3,0	100	0	0	x

All these ions can precipitate ortho P. How well they do so in wastewater seems to be related to some extent to the number of positive charges per Al atom, as illustrated in the penultimate column of the table.



➤ **Figure 7:20** Imagined structure of polymerised Al_{13} ions.

Explanation of the term basicity

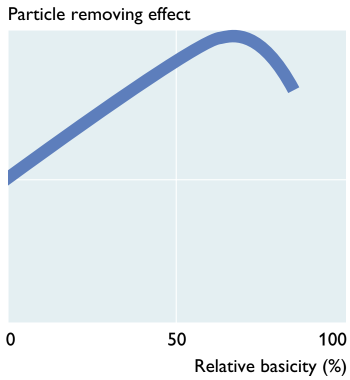
All aluminium salts are acidic, with the exception of aluminate salts that have the chemical formula $Al(OH)_4^-$. This means that hydrogen ions, H^+, are released when they are added to water. A maximum of three H^+ ions can be released for each aluminium ion that is added.

$$Al^{3+} + 3H_2O \rightarrow Al(OH)_3 + 3H^+$$

The generic formula for a pure polyaluminium chloride is $[Al(OH)_xCl_{3-x}]_n$, where $0 < x < 3$ and $n \geq 2$. All polyaluminium salts thus contain OH^-, i.e. "they contain basicity". Cl^- is very loosely bound to the positively charged aluminium ion by electrostatic forces.

The number of H^+ ions that are released per aluminium atom when a polyaluminium salt is added to pure water is 3-x, i.e. less than when a non-basic aluminium salt is added to water.

$$Al(OH)_xCl_{3-x} + (3-x)H_2O \rightarrow Al(OH)_3 + (3-x)H^+ + (3-x)Cl^-$$



➤ **Figure 7:21** The influence of the relative basicity of polyaluminium ions on their ability to remove turbidity and particles.

The **relative basicity** of a polyaluminium salt is defined as moles OH/3 moles Al.

Relative basicity is often expressed in percent, (moles OH/3 moles Al) x100.

Table 7:3 on page 169 shows the molar ratio of OH/Al, the relative basicity of different polyaluminium ions and the number of H^+ ions that are released when aluminium hydroxide is formed from the ions.

The higher the basicity of a polyaluminium salt, the less it will decrease the alkalinity of the treated water and the lower its ability to precipitate orthophosphate ions. Its ability to remove particles and turbidity passes through a maximum as the basicity increases. See figure 7:21.

Basicity is a relatively simple parameter to measure. All polyaluminium salts on the market are characterised by their basicity.

A polyaluminium salt with a given basicity contains a mixture of different simple and polymeric aluminium ions.

Precipitation of particles

Practically all surface forces between small particles (colloids) have a short range that is rarely greater than the size of the particles. This means that they have little influence on the macro-movement of particles, but they are crucial in determining the outcome of collisions between particles, i.e. whether particles join together or bounce off each other.

Neutralisation of charge

Almost all particles in water have a negative charge and therefore repel each other. Particles that repel each other due to their high charge can aggregate when their surface charge is reduced. The surface charge can be reduced by adding (poly)aluminium or iron salts, or other cationic compounds.

Particles in water have different surface properties. A distinction is usually made between hydrophilic and hydrophobic particles. Aluminium and iron(III) salts can aggregate both these types of particles.

Water close to a particle surface

The properties of water close to a particle surface can be very different from those in free water.

The surface of a particle can affect the structure of several layers of nearby water molecules.

The most important effect of water that is bound to a particle surface is to increase the repulsion between approaching particles, since work has to be done to free the water of hydration from the particle surfaces.

It is primarily polymeric metal ions that are adsorbed on to particle surfaces. When a simple aluminium or ferric salt is added to water, the ions must first polymerise before they can be adsorbed.

By adding a pre-polymerised metal salt the particles are encouraged to aggregate faster.

Hydrophobic particles

Hydrophobic particles have a fatty surface. As can be seen from table 7:1 most fat in wastewater exists as particles. Pure fat does not have a charge.

But negatively charged ions, such as chlorides, sulphates and orthophosphates, adhere to hydrophobic surfaces by means of van der Waals forces. Hydrophobic particles in natural water therefore have a negative charge.

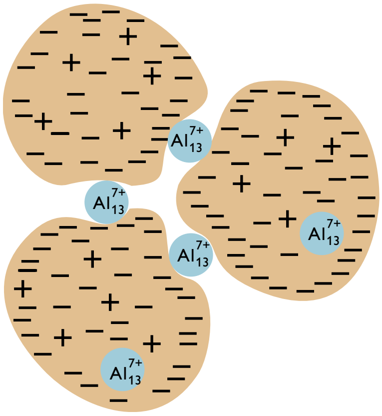
The electrostatic repulsive forces that arise as a result of adsorbed, negatively charged ions can be greater than the van der Waals attraction forces between two hydrophobic particles.

When the negative charge on hydrophobic particles is neutralised, the relatively strong van der Waals attraction forces come into effect. These are inversely proportional to the distance (d) between the particles, with a proportionality ratio that varies between 1/d and $1/d^3$, depending on the roughness of the particle surfaces.

A more hydrophobic particle or dissolved substance, i.e. one that does not have tightly bound water molecules, is naturally adsorbed more easily on to a hydrophobic particle than hydrophilic substances that have a large number of tightly bound water molecules.

Ideal basicity for particle removal

The amount of aluminium that is needed, in the form of a (poly)aluminium salt, to neutralise and aggregate negatively charged particles depends on the basicity of the added polyaluminium salt. Experiments that are described on page 180 have shown that polyaluminium chlorides with a relative basicity of around 65% are most effective at removing turbidity. (See also figure 7:21.)



➤ **Figure 7:22** Precipitation of negatively charged particles by patch adsorption and cross-linking with Al_{13} ions.

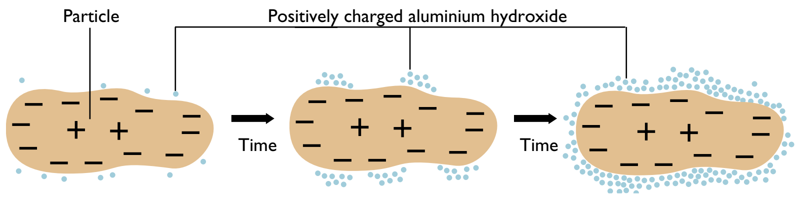
Patch coagulation

It is well known that polymers can aggregate particles through a mechanism known as patch coagulation. The polymers adsorb on to patches on the particles and act as a sort of glue that sticks the particles together. Figure 7:22 illustrates this phenomenon. It is also probable that highly charged polyaluminium ions can aggregate particles in this way.

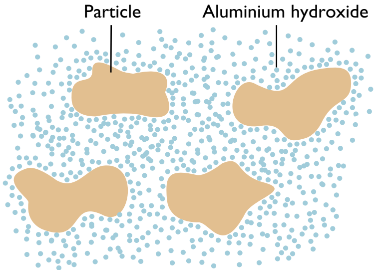
Sweep coagulation

When a (poly)aluminium ion is adsorbed on to the surface of a particle or dissolved substance, layers of hydroxide may start to grow from this area.

This is especially true when the concentration of contaminants is low. The contaminants that are present become enmeshed in the hydroxides. These hydroxides will be present in substantial quantities in the aqueous phase.



➤ **Figure 7:23** Positively charged aluminium hydroxide.



➤ **Figure 7:24** An hydroxide floc with dirt particles.

As they sink, almost all remaining contaminants are swept down with the sinking hydroxides. This type of treatment is called sweep coagulation or sweep flocculation.

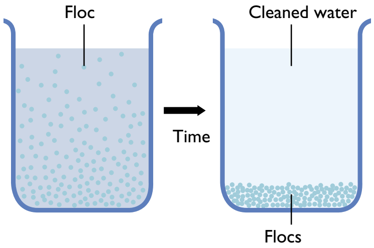
Sweep coagulation is an excellent way of treating water, but the amount of metal salt needed is greater than if the contaminants are removed by charge neutralisation.

Aluminium hydroxide is formed relatively quickly from low basicity aluminium salts. Usually it is formed within 1–7 seconds when a low basicity aluminium salt is added to water.

However, some of the high basicity salts, e.g. those containing $Al_{13}O_4(OH)_{24}(H_2O)_{12}^{7+}$, are very stable in aqueous solutions at certain pH levels and are probably converted first to Al_{13} hydroxides, and after a considerable time to $Al(OH)_3$. As can be seen from the table below, the flocculation time that is needed to treat water to give a predetermined residual turbidity is shorter if a highly basic PAC is used instead of a low basicity PAC.

➤ **Table 7:4** Required flocculation time to achieve a final turbidity of 3 FTU when treating wastewater with 0,45 mmol Al/l in the form of aluminium sulphate, Kemwater PAX-14 and Kemwater PAX-XL19 respectively.

Coagulant	Molar ratio OH/Al of coagulant	Required flocculation time (minutes)
Aluminium sulphate	0	19
Kemwater PAX-14	1,1	10
Kemwater PAX-XL19	2,2	7



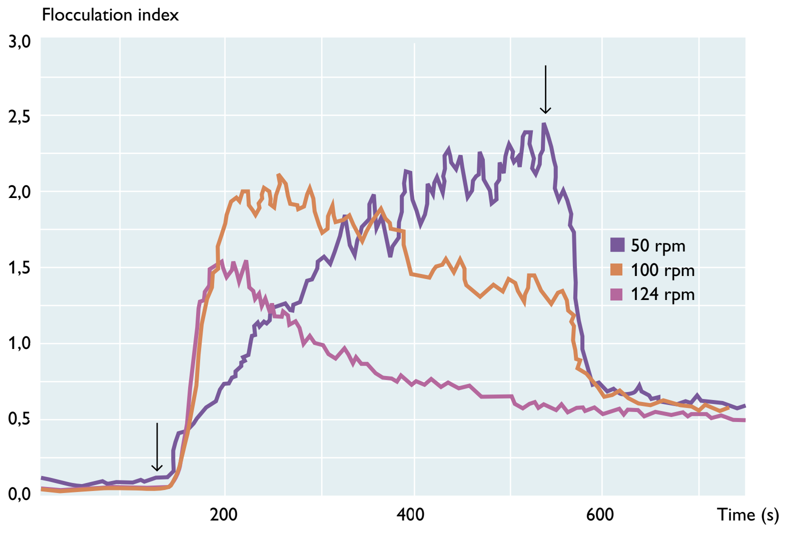
➤ **Figure 7:25** Jar of water with sinking aluminium hydroxide.

Floc size

During the coagulation period, flocs grow to a limited size, depending on pH, temperature, dose, shear rates and the type of coagulant used.
Large flocs are obtained by:

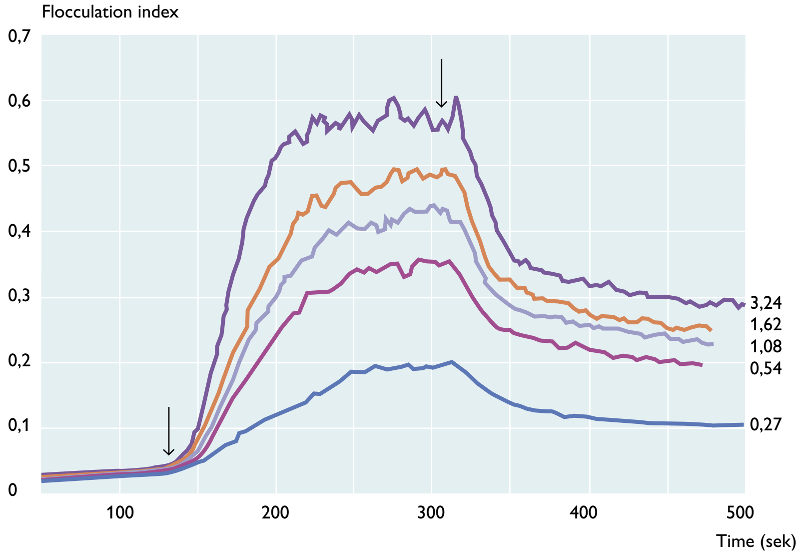
a) using high coagulant doses,
b) carrying out coagulation at relatively low shear rates and
c) using a coagulant with a high basicity.

Figure 7:26 shows the influence of the time and propeller speed used during the coagulation period on the maximum floc size, when a kaolin suspension with an initial pH of about 7,4 was coagulated with Kemwater PAX-XL19.



➤ **Figure 7:26** Influence of time and propeller speed on maximum floc size during coagulation of a suspension of kaolin in mains water from London with 3,1 mg/l Al in the form of Kemwater PAX-XL19. The first arrow shows the time at which the coagulant was added, and the second shows the time at which the propeller speed was increased to 200 rpm.
(Reference: Gregory, J. and Rossi, L., Dynamic Testing of Water Treatment Coagulants, Chemical Water and Wastewater Treatment VI, Hahn. H. H., Hoffman E. and Ødegaard H., (Eds.), Springer-Verlag 2000, pp. 57–65, ISBN 3-540-67574-4.)

Figure 7:27 shows the influence of time and dosage of aluminium sulphate on the maximum floc size (given as the flocculation index) when flocculating an identical kaolin suspension as that described in the previous figure.



➤ **Figure 7:27** Influence of the dosage of aluminium sulphate, given in mg Al/l, on the maximum floc size that is achieved during flocculation of a suspension of kaolin in potable water from London with a propeller speed of 100 rpm. The first arrow shows the time at which the coagulant was added, and the second shows the time at which the propeller speed was increased to 200 rpm.

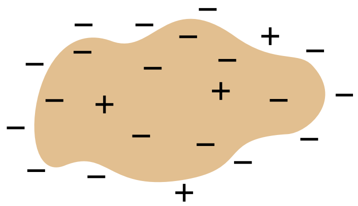
(Reference: Gregory, J., Rossi, L. and Bonnechi, L., Monitoring Flocs Produced by Water Treatment Coagulants, Chemical Water and Wastewater Treatment VI, Hahn H.H., Hoffman E., and Ödegaard H., (Eds.), Springer-Verlag, 2000, pp. 57–65, ISBN 3-540-67574-4.)

The floc size, strength and sedimentation rate can all be increased considerably by adding a flocculation aid (e.g. an anionic polyacrylamide). More information can be found about this on page 204.

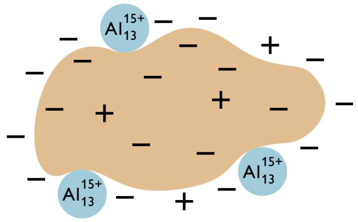
Restabilisation of particles

When particles are neutralised with a high basicity polyaluminium salt, neutralisation takes place within a smaller dosage range than when a non-basic aluminium salt is used. If a high basicity metal salt is overdosed the negatively charged particles may become positively charged before they have had a chance to aggregate. This means that they will remain dispersed, i.e. they are restabilised.

It is therefore easier to overdose with a high basicity aluminium salt than with a low basicity one.



Particle in natural water
having a net negative charge



The same particle with adsorbed Al_{13}^{15+}
now having a net positive charge

➤ **Figure 7:28** Restabilisation. (Reversal of particle charge.)

Different ways of aggregating particles

Aggregation due to particle motion can be caused by:

1. The thermal motion of the water
(Brownian diffusion leading to perikinetic flocculation)
2. Fluid motion (leading to orthokinetic flocculation)
3. Differential sedimentation

The thermal motion of water is only important for aggregating relatively small particles (<0,1 µm) and at low shear rates.

Aggregation due to fluid motion is dominant for particles with a size of about 1 µm and larger.

Differential sedimentation only becomes important when the second particle has a minimum size of about 5 µm.

When two particles approach each other it becomes increasingly difficult for the water to escape from the narrowing gap between them. At distances up to many particle diameters, this **hydrodynamic** or **viscous** effect can still have a retarding effect on particles getting closer to each other. In round figures the collision efficiency for flocculation due to thermal motion (Brownian motion) is halved due to hydrodynamic factors.

For flocculation due to macroscopic fluid motion (orthokinetic flocculation), hydrodynamic effects are more important.

Because of the short times required for hydrolysis, adsorption, precipitation, and flocculation, the exact sequence of events after adding aluminium sulphate are largely unknown.

It is however known that polymeric aluminium and iron(III) ions, and hydroxides of aluminium and iron(III) salts, are adsorbed on to negatively charged particle surfaces, while simple Al^{3+} and Fe^{3+} salts generally lack this ability. (The simple Al^{3+} and Fe^{3+} salts can however precipitate orthophosphate. See page 180.)

At higher particle concentrations, adsorption, charge neutralisation and patch coagulation become more important flocculation mechanisms than sweep flocculation, largely due to kinetic reasons.

Flocs generally grow to a limited size, depending on the coagulant dose, shear rate, shear time, temperature, pH and type of coagulant used.

The influence of polyaluminium salt basicity on the pH value of treated water

All aluminium salts with a basicity below 100% are acidic. This means that the water pH is reduced when an aluminium salt is added. The lower the basicity of the added salt, the more acidic the water becomes. When an aluminium salt with 0% basicity is added to pure water, three H^+ ions are released:

$$Al^{3+} + 3H_2O \rightarrow Al(OH)_3(s) + 3H^+$$

The higher the basicity of the polyaluminium salt, the less the pH of the water will drop.

The number of H+ ions released when a polyaluminium salt reacts with water is directly proportional to the average positive charge on one atom of Al in the salt that is used. See column 5 in table 7:3.

$$Al_{13}O_4(OH)_{24}^{7+} + 11H_2O \rightarrow 13Al(OH)_3 + 7H^+$$

i.e. 7/13 = 0,54 H^+ ions are released per Al atom.

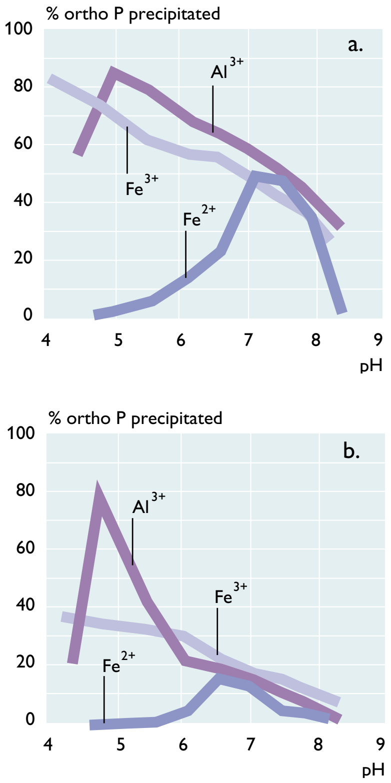
The fact that high basicity aluminium salts only decrease the pH of water slightly is particularly advantageous when treating water with low alkalinity.

Precipitation of orthophosphate with non-basic aluminium and iron salts

It was mentioned earlier that aluminium and iron(III) salts precipitate orthophosphate either by direct reaction or by means of hydroxides. See figures 7:16 and 7:17. As orthophosphate is precipitated more efficiently by direct precipitation it was stressed that the metal salt should be added at a point where the water is highly turbulent.

Iron(II) salts can also be used for the precipitation of orthophosphate. Iron(II) salts precipitate orthophosphate over a considerably more narrow pH range than aluminium and ferric salts.

Figure 7:29a illustrates the influence of pH on the amount of ortho P that is precipitated when 1 mole of Al, Fe(III) and Fe(II) are added to 1 mole of ortho P, while figure 7:29b illustrates the influence of pH on the amount of ortho P that is bound to 20-minute-old hydroxides of the salts.



➤ **Figure 7:29a and 7:29b**
a) The influence of the coagulation pH on the relative percentage of ortho P that is precipitated when solutions of aluminium sulphate, ferric sulphate, or ferrous sulphate are added to solutions of orthophosphate. 1 mole of metal ions was added per mole of ortho P.

b) The influence of pH on the percentage of ortho P precipitated when solutions of ortho P are added to hydroxides that are prepared from the above-mentioned salts. The age of the hydroxides when the ortho P was added was 20 minutes. The pH values of the hydroxide dispersions and the ortho P solutions were identical when they were mixed.

(References: Gillberg, L., Nilsson, D. and Åkesson, M., The Influence of pH When Precipitating Orthophosphate with Aluminium and Iron Salts. In Chemical Water and Waste Water Treatment IV, H. Hahn, E. Hoffman and H. Ødegaard (Eds.) Springer Verlag, 1996, pp. 95-105, ISBN 3-540-61624-1.)

A comparison of the diagrams shows that at most pH values considerably more P is precipitated by the direct precipitation mechanism.

In contrast to both iron(III) and aluminium salts, which precipitate both particles and ortho P, iron(II) salts only precipitate ortho P, not particles.

Calcium salts can also be used for the precipitation of ortho P. When orthophosphate is precipitated with calcium compounds, higher pH values should be used than when using aluminium and iron compounds. Figure 7:30 illustrates the influence of pH on the solubility of iron(III) phosphate, aluminium phosphate and calcium hydroxide phosphate respectively.
(Reference: Leckie H and Stum W. Phosphate precipitation. Water Resources Symposium (1970) 237.)

When calcium hydroxide is used for water treatment comparatively large amounts of sludge are formed.

Precipitation of triphosphate

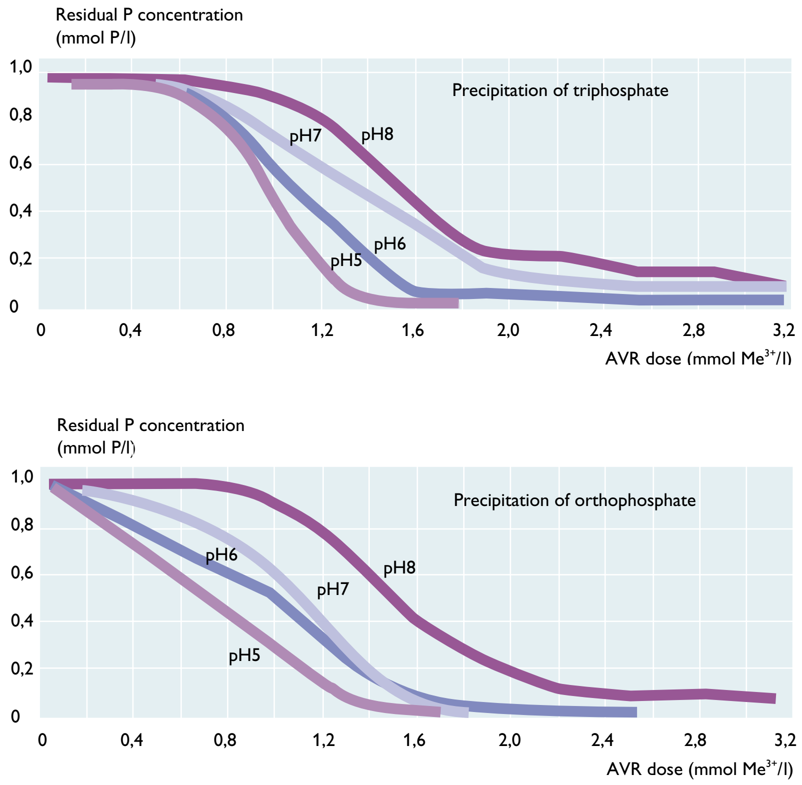
Triphosphate, $P_3O_{10}^{5-}$, sometimes called tripolyphosphate, is used in many detergents. It is used to sequester ions that make water hard. This allows inexpensive anionic surfactants to be used in the detergent.

Triphosphate tends to hydrolyse to orthophosphate with time in the wastewater system. Hydrolysis is usually completed within 3–4 hours in the wastewater system.

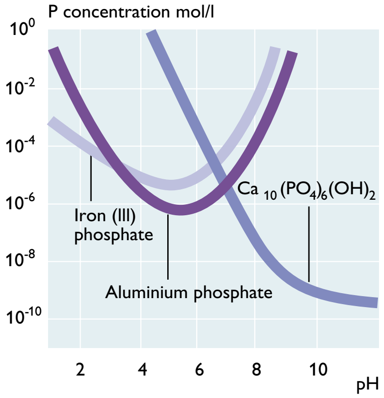
If the time spent in the wastewater pipes is shorter than this the wastewater in the treatment plant may contain triphosphate. Triphosphate can be precipitated using iron and aluminium salts. When a small amount of aluminium or iron salt is added to such wastewater the iron or aluminium will form soluble complexes with the triphosphate. The triphosphate will only precipitate out when it is saturated with aluminium and iron salts.

Figure 7:31a shows the influence of the dose of Kemwater AVR on the residual concentration of triphosphate at different pH values. Figure 7:31b shows the corresponding curves for orthophosphate.

All water that contains complexing agents demonstrates the same special precipitation behaviour. When small to moderate doses of coagulant are added there is no change in the concentrations of phosphate or COD, or in the residual turbidity. It is only when the metal salt dose reaches such a level that the complex-building substances are saturated with coagulant that the water is cleaned to the same degree as if no complex-building substances had been present in the water.



➤ **Figures 7:31a and 7:31b** Influence of AVR dose and pH on residual content of phosphorus during precipitation of triphosphate and orthophosphate from deionised water.

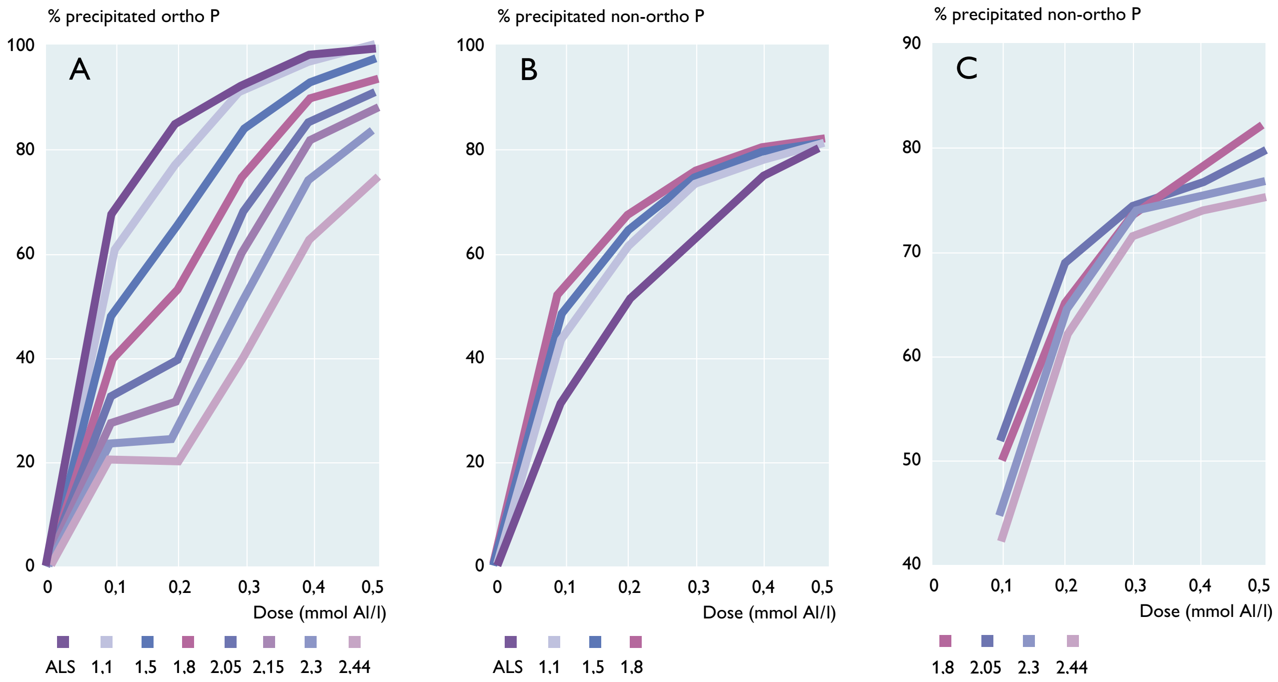


➤ **Figure 7:30** The influence of pH on the solubility of aluminium phosphate, iron(III)phosphate and calcium hydroxide phosphate respectively.

(Reference: Leckie H and Stum W. Phosphate precipitation. Water Resources Symposium (1970) 237.)

The influence of polyaluminium salt basicity on the removal of particles and orthophosphate

There is a basicity that gives the optimum precipitation characteristics. In order to find this basicity, wastewater was precipitated using polyaluminium chlorides with different basicities. A solution of aluminium sulphate was used as a reference salt. The residual concentrations of total phosphorus and orthophosphate were measured. The difference between these two concentrations was then used to calculate the residual concentration of non-ortho phosphorus compounds. As previously mentioned, these are mainly present as particles, e.g. bacteria or virus. The diagram below illustrates the influence of the aluminium dose on these two phosphorus fractions.



➤ **Figure 7:32** Influence of the dose of aluminium sulphate and polyaluminium chloride with various molar ratios of OH/Al on the percentage concentration of precipitated orthophosphate and the percentage concentration of precipitated phosphorus that did not come from orthophosphate (mainly particles). Diagram A shows the percentage concentration of precipitated orthophosphate. Diagram B shows the percentage concentration of precipitated non-ortho P for various doses of aluminium sulphate and polyaluminium chlorides (PAC) with molar ratios of OH/Al in the range 1,1–1,8. Diagram C shows the percentage concentration of non-ortho P precipitated using PAC with molar ratios of OH/Al in the range 1,8–2,44. Diagram C has an expanded scale on the y-axis compared with diagram B.

(References: Gillberg L., Influence of the Basicity of Polyaluminium Chlorides When Cleaning Municipal Wastewater, In: Chemical Water and Wastewater Treatment III, Klute R., and Hahn H.H., (Eds), Springer-Verlag, Berlin, Heidelberg, 1994, pp. 39–56, ISBN 3-540-58185-5.)

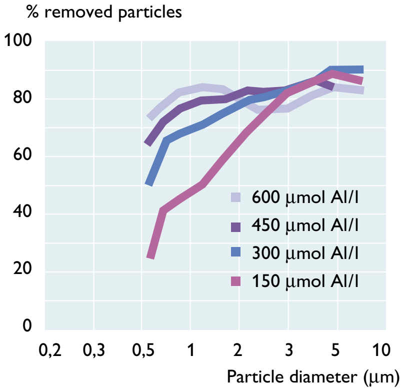
It can be seen from diagram C that the salts with a molar ratio of OH/Al between 1,8–2,05, which corresponds to a relative basicity of around 60–68%, were most effective at precipitating particles.

It can also be seen that the ability to precipitate orthophosphate decreases with increasing basicity of the salt.

The lowest dose of aluminium sulphate precipitated almost 70% of the ortho P, but only 30% of the non-ortho P. The lowest dose of aluminium sulphate thus precipitated more ortho P than particles. The lowest dose of PAC with a molar ratio of 2,05 precipitated little more than 50% of the non-ortho P and only 35% of the ortho P. The lowest dose of this PAC thus precipitated more particles than ortho P.

Both monomeric and polymeric ions of Al and Fe can precipitate orthophosphate. It has been shown that iron ions must be polymerised in order to be bound to a particle surface. This is probably also true for polyaluminium salts. Of the two differently charged iron ions it is only Fe^{3+} that can be polymerised. In order for iron or aluminium ions to be polymerised the concentration of iron or aluminium ions must be sufficiently high and the pH must be within an acceptable range. This explains why the low basicity aluminium salts initially precipitated orthophosphate, and only began precipitating out large amounts of particles after a considerable amount of othophosphate had been precipitated. The reverse situation applies to high basicity aluminium salts. They began by precipitating particles. They did not precipitate large amounts of orthophosphate until after a considerable amount of particles had been precipitated.

From figure 7:33 it can be seen that a given dose of coagulant precipitates relatively more large particles than small particles. In order to precipitate the majority of small particles, e.g. bacteria or viruses, it is important that a sufficient dose of coagulant is added.



➤ **Figure 7:33** The influence of the dose of aluminium sulphate on the percentage of particles precipitated in different size classes.

(References: Gillberg L., Eger L. and Jepsen S.-E. The effect of Five Coagulants on the Concentration and Distribution of Small Particles in Sewage. In: Chemical Water and Wastewater Treatment, Hahn H.H., and Klute R., (Eds.) Springer-Verlag Berlin, Heidelberg 1990, pp. 243–256, ISBN 3-540-53181-5.)

The influence of pH on the coagulation process

The pH value is a very important parameter in water treatment processes.

The surfaces of particles in water contain groups that change their charge with pH. Proteins in particular contain groups that vary their charge with pH. All viruses and many bacteria have a surface made of protein.

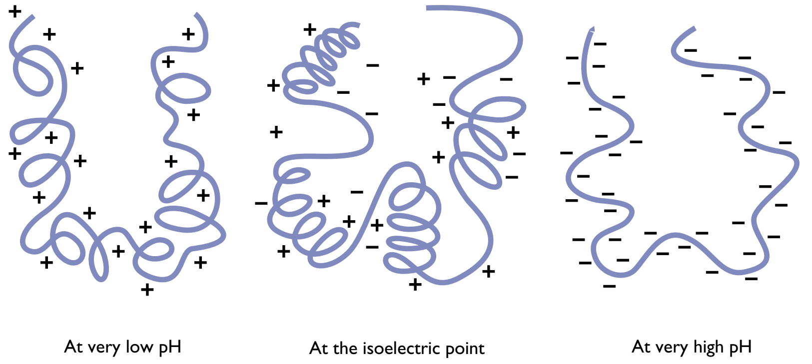
Some groups on the surface of proteins have zero charge at low pH levels and have a negative charge at higher pH levels, e.g. carboxylic (-COOH ↔ -COO-, pK_a approx. 2–5), sulphhydryl (-SH ↔ -S-, pK_a approx. 8–9), hydroxyl and phenolic groups (-OH ↔-O-, pK_a approx. 10–11).

The pK_a value is the pH at which both forms exist in equal amounts. The actual pK_a value of these groups depends on the type of group that is adjacent to the functional group.

Proteins also contain groups which at acidic to neutral pH are positively charged and at basic pH have zero charge, e.g. amino groups ($-NH_2^+ \leftrightarrow -NH_3$, pK_a approx. 9–11), guanidino- ($=NH_2^+ \leftrightarrow =NH$, pK_a approx. 12,5) and imidazole groups ($=NH^+ \leftrightarrow =NH:$, pK_a approx. 6).

The charge on a particle with a protein surface is strongly dependent on pH. With increasing pH the number of negative charges increases and the number of positive charges decreases, and with decreasing pH the number of positive charges on the surface increases and the number of negative charges decreases. The pH at which there are an equal number of positive and negative charges on the protein is called the isoelectric point of the protein. Different proteins have different isoelectric points, and many proteins coagulate spontaneously at their isoelectric point.

The higher the pH, the more negative charge the surface of the protein will have, and the more positive charges will be needed to neutralise and precipitate the protein, i.e. the more metal salt will need to be added. pH influences both the charge on hydroxides and particle surfaces, and the type and rate at which polyiron or polyaluminium ions are formed.



➤ **Figure 7:34** Charge on a globular protein at different pH levels. It can be seen from the figure that the configuration of proteins also changes with pH.

When the added (poly)metal ions react with the contaminants in the water it does not affect the pH of the water. But when an aluminium or ferric salt reacts with the water molecules and forms hydroxides the pH will drop. Because there are so many more water molecules to react with compared to the number of contaminants, the pH will always drop when an iron or aluminium salt is added to water.

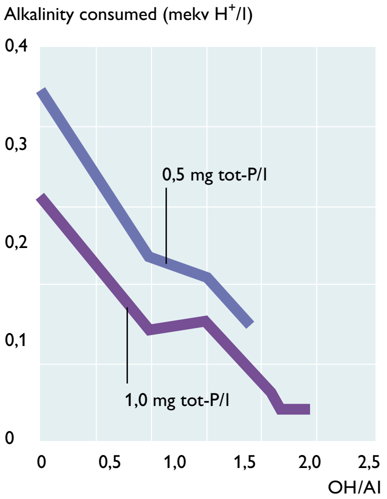
The magnitude of the pH drop depends on the basicity of the salt used and the alkalinity of the treated water. If a salt with low basicity is used, the metal ions must polymerise before they react with a particle surface. When iron or aluminium ions are polymerised they release H^+ and the pH drops. This means that a low basicity coagulant will lower the pH/alkalinity considerably more than a high basicity coagulant when they are used to treat water to the same COD/TOC level. This is illustrated in figures 7:35 and 7:36.
(References: Gillberg L., Influence of Polyaluminium Chlorides When Cleaning Municipal Wastewater, In: Chemical Water and Wastewater Treatment III, Klute R., and Hahn H.H., (Eds.) Springer-Verlag, Berlin, Heidelberg, 1994 pp. 39–56, ISBN 3-540-58185-5.)

The less coagulant that is used, the more important it is to have good control of the pH. The higher the dose of coagulant used, the less important it is to control the pH. This effect is shown in figure 7:37.

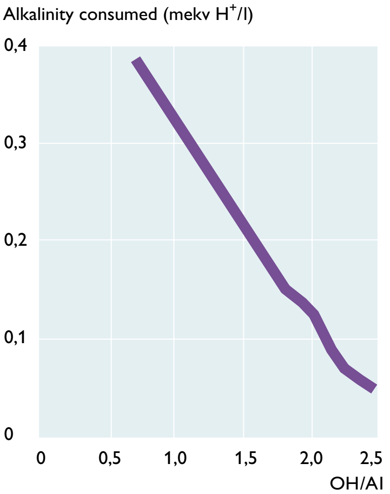
Different coagulants have their optimum treatment efficiency at different pH levels.

Iron(III)salts often work better at lower pH than aluminium salts.

With high basicity coagulants, water can be treated at higher pH levels than with the corresponding lower basicity coagulants. The reason for this is that high basicity polyaluminium ions are often more stable and therefore retain their high positive charge for longer than low basicity ions.



➤ **Figure 7:35** The influence of the molar OH/Al ratios of PAC on the alkalinity consumed when wastewater was treated to give two constant residual phosphorus concentrations.



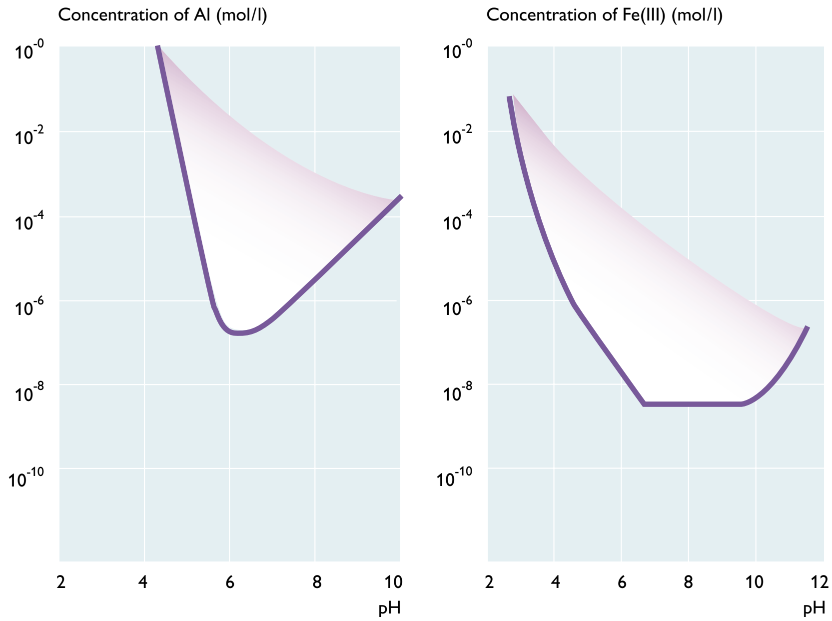
➤ **Figure 7:36** The influence of the molar OH/Al ratio of PAC on the alkalinity consumed when wastewater was treated to give a constant residual concentration of 14 mg TOC/l.

The presence of other groups (ligands) than OH^- in the polysalt also strongly influences the pH for optimum coagulation. More about this in a later section.

➤ **Figure 7:37** Influence of pH on residual colour when coloured surface water is treated with different doses of aluminium sulphate.

The influence of pH on the solubility of iron(III) and aluminium salts

Drinking water should have a low residual content of aluminium and iron. The residual concentrations of Al^{3+} or Fe^{3+} in surface water after treatment with aluminium or iron salts depend on the pH. Figure 7:38 shows the influence of pH on the solubility of aluminium and Fe(III) salts.

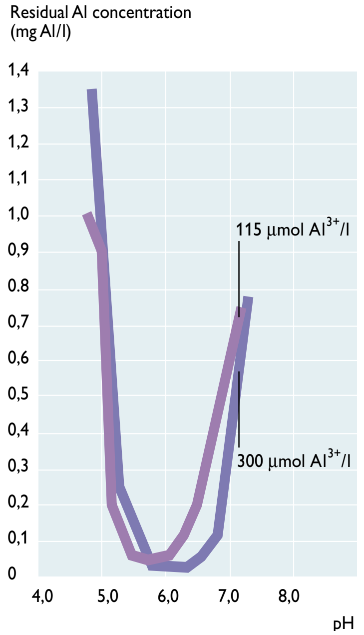


➤ **Figure 7:38** Influence of pH on the solubility of aluminium and ferric salts.

Naturally occurring water often contains ions of different kinds, such as sulphate, calcium or magnesium ions. These ions (and many others) adhere to iron or aluminium hydroxides and thereby change their charge. They therefore displace the pH at which the salt that is used has its lowest solubility. Adsorbed anions displace the value in the acidic direction, while cations displace it in the basic direction.

The pH that gives the lowest residual concentration of aluminium or iron should therefore be determined experimentally for each water and type of metal salt. This should be done at the actual water temperature, as this also influences the solubility of the salt. Solubility decreases with decreasing temperature.

The dose of metal salt that is added to contaminated water influences the pH at which the lowest residual iron or aluminium concentration is obtained. Increasing the amount of metal salt that is added increases the pH range that gives the lowest residual iron or aluminium concentration, while also displacing it in the basic direction. See figure 7:39.

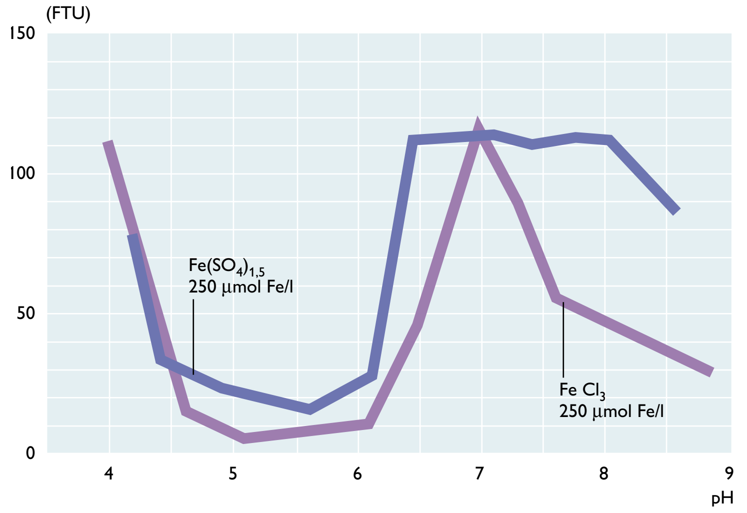


➤ **Figure 7:39** The influence of pH on the residual aluminium concentration when a humic water was treated with different doses of aluminium sulphate.

The influence of negatively charged counter ions in aluminium or iron(III)salts

All metal salts contain negatively charged counter ions. Aluminium and ferric sulphates and chlorides, and mixtures of the two, are available on the market. The choice of counter ion affects the results of the treatment process. This is because the sulphate ions bind to aluminium and iron(III) hydroxides, and thus reduce their positive charge. Chloride ions do not bind to aluminium ions and only to a small extent to iron(III) ions. In addition, sulphates, but not chlorides, can to some extent bind to positively charged sites on particles and hence give the particle an even higher negative charge than it would have had in the absence of sulphate. Both these phenomena mean that a higher dose of an iron(III) sulphate may be needed to precipitate particles than is the case for an iron(III) chloride.

These phenomena also mean that water can be treated at a slightly higher pH with a chloride salt than with a sulphate salt. This is shown in figure 7:40.

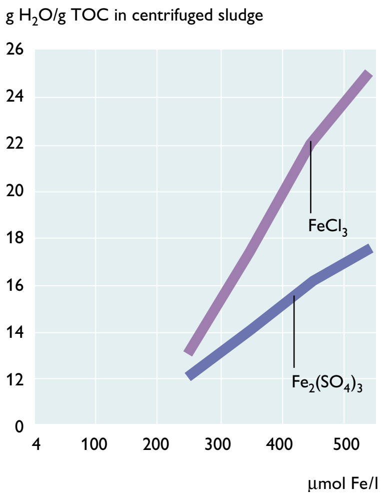


➤ **Figure 7:40** Influence of pH on the residual turbidity of synthetic wastewater treated with iron in the form of ferric chloride and ferric sulphate, respectively.

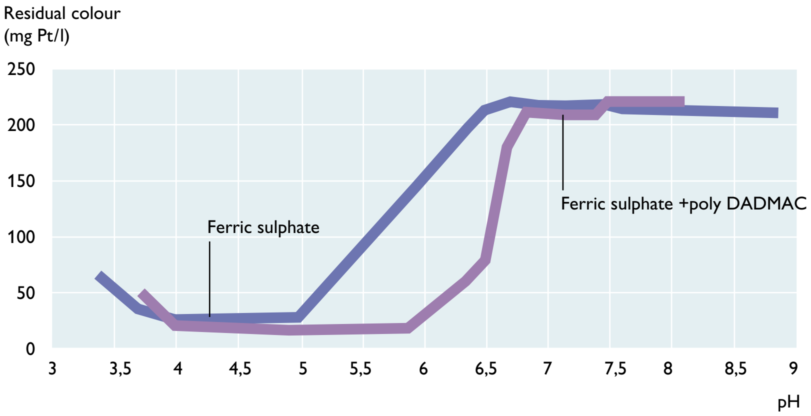
Orthophosphate ions, on the other hand, are precipitated just as efficiently by iron(III) sulphate as by iron (III)chloride. This is because othophosphate is bound more strongly to hydroxides than to sulphate. When orthophosphate ions are bound to iron(III)hydroxide formed from iron(III)sulphate it releases some of the sulphate ions being adsorbed by the hydroxide.

The sludge that is formed during treatment with aluminium salts and iron salts is relatively bulky. One of the explanations is that hydroxides of iron and aluminium are positively charged. Different flocs repel each other and the space between them is filled with water. Since flocs produced by sulphate salts have a lower positive charge than those produced by chloride salts, the flocs produced by sulphate salts can get closer to each other and the resulting sludge is more compact than that produced by chloride salts. This effect is illustrated in figure 7:41, which shows the water content of centrifuged sludge obtained during treatment of synthetic wastewater with ferric chloride and ferric sulphate respectively.

If you want to use a ferric sulphate to treat water efficiently at pH levels at which only ferric chloride works, you could try mixing a small dose of a cationic polymer with the sulphate salt. The extra positive charge on the cationic polymer permits treatment at higher pH levels. This effect is illustrated in figure 7:42.



➤ **Figure 7:41** The influence of the amount of iron added to synthetic wastewater as ferric chloride and ferric sulphate respectively on the weight of water per gram of organic carbon in the centrifuged sludge.



➤ **Figure 7:42** Influence of pH on residual colour when coloured soft water was dosed with 0,115 mmol of iron in the form of ferric sulphate, with and without a small amount of poly-DADMAC. The water samples were filtered through a filter with pore openings of 0,45 µm before measurement.

The influence of silicate and sulphate in polyaluminium salts

Several procedures are available today for introducing various ligands into polyaluminium ions.

Polyaluminium chlorides with various sulphate contents are available on the market. The sulphate ions speed up floc formation and help give a low residual aluminium content in the treated water. When sulphate is incorporated in iron or (poly)aluminium chloride it displaces the pH for optimum treatment towards the acid direction, i.e. towards a lower pH.

Procedures also exist for incorporating silicate groups in polyaluminium ions. Coagulants with moderate basicity that contain silicates have a good particle reduction effect, similar to that of high basicity coagulants.

The incorporation of silicate or sulphate ions in polyaluminium ions facilitates precipitation of substances that are otherwise difficult to precipitate.

The removal of toxic ions with the aid of hydroxides

As previously mentioned, hydroxides are charged and their charge depends on the pH and the salt from which they were prepared. At pH levels that are neutral to acid, hydroxides have a positive charge, but at higher pH they gain an increasing number of negative charges and eventually become negatively charged.

Ions of opposite charge bind to the charged hydroxides. This fact can be used for the removal of toxic ions.

There is a specific pH range within which coagulation can take place.

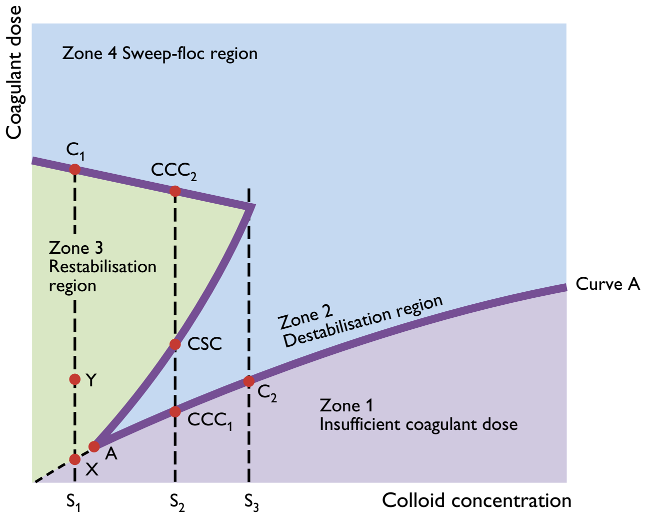
If you want to remove positively charged toxic ions, flocculation should be carried out at as high a pH as possible. At high pH levels, the hydroxides gain a greater number of negative charges and can then bind positively charged ions, which then accumulate in the sludge.

If on the other hand you want to remove a negatively charged toxic ion, flocculation should be carried out at as low a pH as possible.

How the concentration of contaminants affects coagulant dosage

Figure 7:43 is useful for understanding how much coagulant is required to precipitate different concentrations of contaminants.

It illustrates what happens when different doses of iron(III) sulphate or aluminium sulphate are added to different amounts of a silicate/bentonite suspension at a pH of around 4–5. Those who are interested can find similar diagrams for other pH levels in the reference.



Zone 1 – illustrates the region in which too little coagulant has been added in order to neutralise the negative charges on the particles.

Zone 2 – illustrates the region in which a sufficient dose has been added in order to neutralise and flocculate the particles. This type of treatment often produces less sludge than treatment by sweep coagulation.

Zone 3 – illustrates the region in which the coagulant concentration is so high that the particles have such a high positive charge that they repel each other and do not aggregate.

Zone 4 – sweep coagulation region.

➤ **Figure 7:43** Influence of the concentration of colloidal particles on the amount of coagulant that gives different effects at a precipitation pH of roughly 5.

(Diagram taken from page 101 of the book "Coagulation and Flocculation" by John Bratby (Upland Press Ltd, 1980). This is a reassessment of a study by Stumm and O'Melia (Stumm, W. and O'Melia, C.R. 1968. Stoichiometry of coagulation, J. Amer. Waterworks Association., 60:514-539.)

Suppose that we have relatively clean water that we want to treat with a coagulant, and that the particle concentration is at level S1 in the diagram. From the diagram it can be seen that a very low coagulant concentration is needed and that this concentration has such a narrow range that it is impossible to add the right dose. In this case it is necessary to add such a high dose of coagulant that you reach the sweep floc range.

One way out in cases such as this is to mix a little of the sludge formed during the treatment process with the water to be treated. This increases the particle concentration so that a lower dose of coagulant can be used.

More commonly, however, the contaminant concentration is as shown by S_2. The coagulant concentration CCC_1 is the lower critical coagulant concentration, CSC is the critical stabilisation concentration, and CCC_2 is the upper critical coagulant concentration.

All these concentrations depend on pH, temperature and the type of coagulant used.

When polymerised metal ions are adsorbed directly, the particles flocculate by "adsorption flocculation".

When the electrolyte concentration rises above CSC and reaches CCC_2, the particles coagulate again.

Treating water with low alkalinity

When a coagulant, e.g. aluminium sulphate, is added to water with low alkalinity, the pH of the water may drop so fast that it is difficult to treat the water at a reasonably stable pH. The various polyaluminium ions, which would otherwise have formed at certain pH levels, may not have time to develop.

One method that can be used in a case like this is to add a little hydrogen carbonate or carbonate to the water. The carbonate stabilises the pH after the coagulant has been added. This makes it possible to decrease the dose of coagulant needed.

The source of carbonate should be chosen on the basis of cost and effectiveness. Candidates include $NaHCO_3$, Na_2CO_3 or $CaCO_3$, possibly in combination with CO_2 addition.

This method will not work if the sulphate concentration of the water is high (approx. 100 mg/l).

More information about the effect of hydrogen carbonate can be found in a paper by Letterman et al.

(Reference: Letterman, D.L., Tabatabaie, M. and Ames R.S. Jr. The Effect of the Bicarbonate Ion Concentration on Flocculation With Aluminum Sulfate, Journal AWWA, August 1979. 467–472.)

Properties of Kemwater's metal salts

Different aluminium and iron salts with various basicities and counter ions are produced by Kemwater.

The types of salt that are produced in different countries depend on the availability of raw materials and the nature of the water to be treated.

Kemwater has developed methods that make it possible to produce coagulants with a low heavy metal content regardless of the type of raw material. Some of Kemwater's coagulants are among those with the lowest heavy metal content available on the market.

Tables 7:5 and 7:6 summarise the types of metal salts that contain aluminium and iron and are produced by Kemwater. They also show the typical concentrations, basicities and main applications. Kemwater also produces salts other than those mentioned in tables 7:5 and 7:6.

It generally can be said of aluminium salts that:

- **The higher the basicity of the coagulant, the less it reduces the pH of the water.**

- **Of the above coagulants the least amount of sludge seems to be produced by medium basicity polyaluminium chlorides and aluminium sulphate.**

- **The ability of PAC to reduce turbidity is greatest when the basicity is around 65%.**

- **When the coagulant contains sulphate or silicate, floc formation proceeds more rapidly than in the absence of these ions.**

- **When a coagulant contains sulphate or silicate the optimum pH for flocculation is displaced slightly in the acidic direction.**

- **When the coagulant includes an organic polymer, treatment can be carried out over a wider pH range.**

- **Bad-smelling hydrogen sulphide is produced by bacterial reduction of sulphate ions. As long as the wastewater contains nitrate the bacteria prefer to oxidise this into nitrogen gas and do not oxidise the sulphate ions. No hydrogen sulphide is formed in this case. Aluminium nitrate is therefore useful for odour control. In contrast to ferric nitrates it does not produce a black precipitate.**

- **Nitrate salts can be used to stimulate the biological decomposition of organic substances. By using nitrate salts effluents with a lower residual content of organic material can be produced.**

➤ **Table 7:5** Typical content of various aluminium salts produced by Kemwater.

Brand name	Active ingredient	Al %	Basicity %	Form	Main use and characteristics
Kemwater ALG	Aluminium sulphate	9,1	3	Granules Paper sizing	Surface water treatment
Kemwater ALS	Aluminium sulphate	4,3	3	Liquid Paper sizing	Surface water treatment
Kemwater AVR	Aluminium and ferric sulphate	8,1 and 0,7% Fe	3	Granules	Mainly wastewater treatment
Kemwater PAX-10 and PAX-11	Polyaluminium sulphate chloride	5	41	Liquid	Wastewater and surface water treatment
Kemwater PAX-12 to 19	Polyaluminium chloride	5,6–9,8	30–40	Liquid	Wastewater and surface water treatment
Kemwater PAX-16S	Polyaluminium chloride	15,0	37	Granular powder	Wastewater and surface water treatment
Kemwater PAX-20 series	Polyaluminium and ferric chloride		35–40	Liquid	Wastewater treatment
Kemwater PAX-XL1 and PAX-XL3	Polyaluminium chloride	5,3	70	Liquid	Wastewater and surface water treatment. Excellent turbidity and colour removal. Less effective for ortho P removal. Works over a wide pH range
Kemwater PAX-XL9 and PAX-XL10	Polyaluminium sulphate chloride	4,5–5,1	70	Liquid	Similar to Kemwater PAX-XL1 but forms flocs faster
Kemwater PAX-XL19	Polyaluminium chloride	12,4	80	Liquid	Similar to Kemwater PAX-XL1 but forms larger flocs and gives even less acidity to the water
Kemwater PAX-XL30 series	Polyaluminium chloride with organic polymer	5–11,8	30–70	Liquid	Similar to Kemwater PAX18 but gives better TOC reduction and often a lower sludge volume
Kemwater PAX-XL60	Polyaluminium silicate chloride	7,5	40	Liquid	Similar to Kemwater PAX-XL1 but decreases the pH of the treated water to a higher extent
Kemwater PAX-XL60S	Polyaluminium silicate chloride	15,4	40	Granular powder	Spray-dried variant of Kemwater PAX-XL60
Kemwater PAX-XL61	Polyaluminium silicate chloride	5,4	70	Liquid	Similar to Kemwater PAX-XL60 but decreases the pH of the treated water to a lower extent
Kemwater PAN-1	Aluminium nitrate	4,3	0	Liquid	Wastewater treatment Good for odour control
Kemwater PAN-4	Polyaluminium nitrate	7,2	35	Liquid	Wastewater treatment Good for odour control

It generally can be said of iron salts that:

- **The chloride salts work over broader pH ranges than the sulphate salts. Sometimes a lower concentration of iron is needed in the form of a chloride salt than of a sulphate salt to achieve a given effect.**
- **The sludge volume produced by a constant dose of iron added in the form of a sulphate salt is lower than that produced by the same amount of iron added as a chloride salt.**
- **Poly-ferric sulphate decreases the pH of the treated water to less of an extent and has roughly the same treatment efficiency as ferric sulphate.**
- **When a ferric nitrate salt is used it combats the odour from sulphur compounds in two ways. As long as the wastewater contains nitrate this is oxidised to nitrogen gas and no bad-smelling hydrogen sulphide is formed. In addition to this the ferric ions precipitate sulphide through redox reactions in the form of FeS, which is black in colour.**
- **Ferric salts decrease the pH of the treated water more than aluminium salts.**
- **Ferric salts often work best at a slightly lower pH than aluminium salts.**

➤ **Table 7:6** Typical concentrations of iron salts produced by Kemwater.

Brand name	Active ingredient	Fe %	Basicity %	Form	Main use and characteristics
Kemwater COP	Ferrous sulphate	18		Crystals	Wastewater treatment
Kemwater PIX-110	Ferric chloride sulphate	12,1	–	Liquid	Wastewater and surface water treatment
Kemwater PIX-111	Ferric chloride	13,4	–	Liquid	Wastewater and surface water treatment
Kemwater FERIX-3	Ferric sulphate	20,5	–	Granules	Wastewater and surface water treatment
Kemwater FIN-12 and 22	Ferric nitrate sulphate	11,0	–	Liquid	Wastewater treatment Effective for odour removal
Kemwater PIX-112 to 115	Ferric sulphate	11,8	–	Liquid	Wastewater and surface water treatment
Kemwater PIX-122 / 123	Poly-ferric sulphate	12,6	11	Liquid	Wastewater and surface water treatment
Kemwater PIX - 131 and PIX-132	Ferric salts with organic polymer	10–13	–	Liquid	Wastewater and surface water treatment
Kemwater PIX-300-series	Ferric salts with very low heavy metal content	11,5		Liquid	Surface water treatment

Tables 7:5 and 7:6 should only be used as a guide. Laboratory experiments with different coagulants should always be carried out in order to choose the most suitable product.

In addition to the products described in tables 7:5 and 7:6 Kemwater has several products under development that are currently being tested in various markets.

Organic polymers

Polymers are made up of repeating units of one or more chemical units.

Monomers are used for the production of polymers.

Most polymers used in water treatment are linear polymers, i.e. polymers without branches.

The repeating units can be of the same type, e.g. AAAAAAAAAAAAAAAAA. These are called **homopolymers**.

Polymers can also be built up of different types of repeating units, e.g. AAAABBAABBBAAAABABBAAA etc.

A = one type of repeating unit
B = another type of repeating unit

Polymers with different types of repeating units are called **copolymers**.

There are also polymers in which one or more of the repeating units has a charge. These polymers are called **polyelectrolytes**.

Polymers that contain positively charged groups are called **cationic polymers**, and polymers with negatively charged groups are called **anionic polymers**.

Many types of cationic polymers can be mixed with aluminium and ferric salt solutions.

Anionic polymers should not be mixed with metal salts, since the metal ions react and can form precipitates with anionic polymers.

Polymers with repeating units with no charge are called **non-ionic polymers**.

Polymers can be manufactured with a different number of repeating units (**degree of polymerisation**). The highest number of repeating units varies greatly between different types of polymers. The molecular weight of polymers therefore varies widely, from a couple of hundred to tens of millions.

Besides neutralising the charge on particles, polymers can bridge charged particles, rather like adhesive tape binding two or more objects together. An anionic polymer that is added after a brief period of coagulation with a metal salt cross-links the flocs so that they become much stronger than flocs formed with a metal salt alone. Flocs that are formed with anionic polymers can be subjected to high shear rates without breaking up.

Some applications, such as dewatering an active sludge in a centrifuge, require polymers that have a strong bridging action. A polymer with a high molecular weight should be chosen for such applications.

Some other applications require a polymer with a less pronounced bridging action. A polymer with a lower molecular weight should be chosen in such cases.

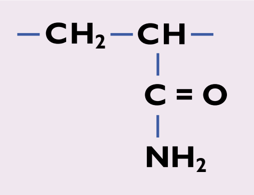
Below is a description of the chemical composition and some typical applications of different polymers.

Polyacrylamides

Polyacrylamides are made from the monomer acrylamide:

$CH_2{=}CH{-}CONH_2$

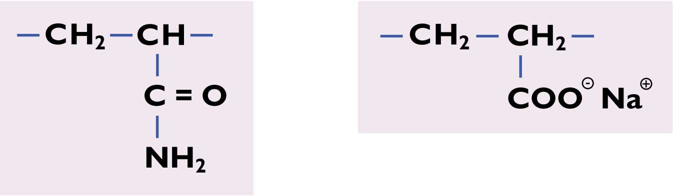
Polyacrylamides are among those polymers that can be produced with a very high molecular weight. Low molecular weight polyacrylamides can also be produced.



$$-CH_2-\underset{\underset{NH_2}{|}}{\underset{C=O}{|}}{CH}-$$

➤ **Figure 7:44** The repeating unit in non-ionic polyacrylamide.

Acrylamide can be copolymerised with acrylic acid ($CH_2{=}CH{-}COOH$) or sodium acrylate. This results in negatively charged polyacrylamides.



➤ **Figure 7:45** The non-ionic and negatively charged repeating unit in anionic polyacrylamides.

Negatively charged polyacrylamides are mainly used for speeding up floc formation, strengthening and condensing flocs and for reducing the water content of chemical sludge.

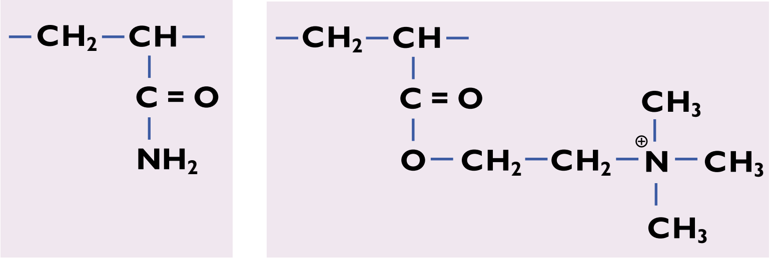
When water is treated with an aluminium or iron salt the flocs contain positively charged hydroxides. The negatively charged groups of the polyacrylamide bind to the positively charged sites on the flocs and link them together. The flocs become denser, sink faster, are stronger and contain less water than flocs formed without the addition of negatively charged polymers.

When flocculation is carried out in combination with a negatively charged polymer it is also possible to use considerably shorter flocculation times than when the water is treated solely with a metal salt. (More information about this can be found on page 204.)

Acrylamide can also be copolymerised with different types of cationic vinyl amines, e.g. quaternary DMAEA.

$CH_2{=}CH{-}COO{-}CH_2CH_2{-}N^+(CH_3)_3Cl^-$

This produces a cationic polyacrylamide.



➤ **Figure 7:46** The non-ionic and positively charged repeating unit in many cationic polyacrylamides.

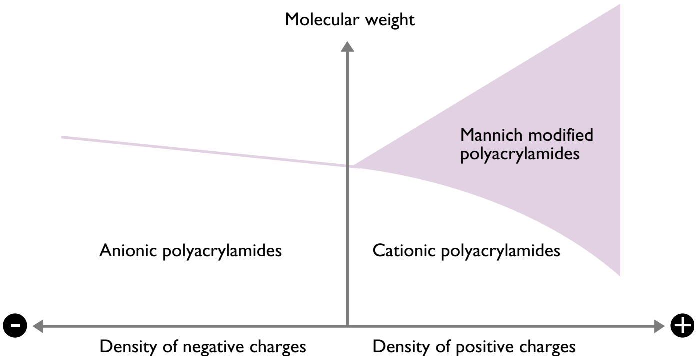
Cationic polyacrylamides are used, among other things, for the dewatering of sludge from biological treatment processes.

The sludge particles have negative charges. The cationic groups of the polyacrylamide bind to the negatively charged sites on the sludge particles and link them together, allowing the sludge particles to get closer to each other. This means that the water is squeezed out and the sludge becomes drier.

Negatively charged polyacrylamides can be produced both with a high molecular weight and with a high charge density.

When positively charged polyacrylamides are polymerised the maximum molecular weight of the resulting polymer decreases with increasing cationic charge density.

The diagram in figure 7:47 illustrates the influence of the density of negative and positive charges respectively on the highest molecular weight at which polyacrylamides can be produced.



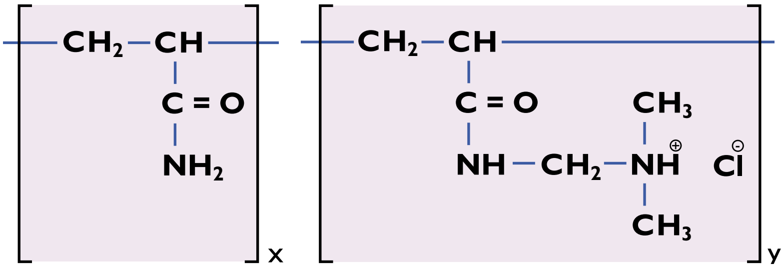
➤ **Figure 7:47** Influence of the charge density of a polyacrylamide on its maximum molecular weight.

From the above diagram it can be seen that it is not possible to produce high molecular weight polyacrylamides with a high positive charge density by means of a direct polymerisation reaction.

It is however possible to add positively charged groups to a non-ionic polyacrylamide by means of a Mannich reaction. This makes it possible to produce polyacrylamides with a high molecular weight and high density of positively charged groups. Aqueous solutions of such polymers are highly viscous and have a low polymer content. This makes them expensive to transport over longer distances.

The higher the charge density, the more elongated the polymer will be in water and the higher the viscosity of the aqueous solution.

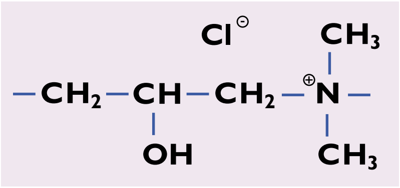
Mannich polymers are excellent for dewatering biological sludges in centrifuges.



➤ **Figure 7:48** Repeating units in Mannich-processed polyacrylamides.

Polyamines

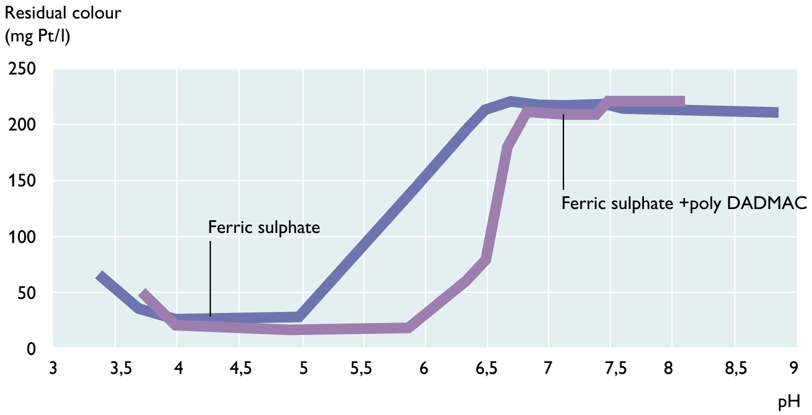
There are different types of amines, including those with the following repeating unit.



➤ **Figure 7:49** Repeating unit in a quaternary polyamine.

Polyamines can be mixed with aluminium and iron salts. By using such a mixture it is possible to lower the TOC content of water despite using a lower metal dose. A drier sludge is obtained at the same time.

If a cationic polymer is mixed with an iron salt or aluminium salt it allows the water to be treated at a higher pH, as illustrated in figure 7:42.



➤ **Figure 7:42** Influence of pH on residual colour when coloured soft water was dosed with 0,115 mmol of iron in the form of ferric sulphate with and without a small amount of poly-DADMAC. The water samples were filtered through a filter with pore openings of 0,45 μm before measurement.

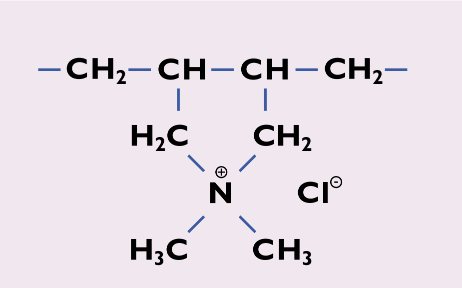
It is possible to reduce the turbidity of water that has very high turbidity levels, > approx. 500 FTU, by using cationic polymers alone. However, to reduce the turbidity of water that has low to high turbidity levels, a metal salt must be used, possibly in combination with a cationic polymer.

When a cationic polymer is used, the dose of metal salt can be reduced in comparison with that required when water is treated with a metal salt alone.

Polymers are more expensive per positive charge than iron and aluminium salts. One should therefore evaluate the overall cost situation.

Poly-DADMAC (Polydiallyl dimethyl ammonium chloride)

Poly-DADMAC can be mixed with aluminium and iron salts, and has the same range of applications as other polyamines.



➤ **Figure 7:50** Repeating unit in poly-DADMAC.

Polyethylene imines

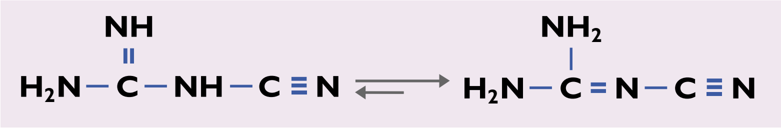
Polyethylene imines are branched polymers with the repeating unit:

$-CH_2-CH_2-NH-$

Polyethylene imines have roughly the same range of applications as poly-DADMAC and other polyamines. They are not used as widely as they are relatively expensive and the monomer is toxic.

Dicyandiamide polymers

Dicyandiamide, often abbreviated to dicy, is also known as cyanoguanidine.
At least two forms of the monomer exist:



$$H_2N-\overset{NH}{\overset{\|}{C}}-NH-C\equiv N \rightleftarrows H_2N-\overset{NH_2}{\overset{|}{C}}=N-C\equiv N$$

➤ **Figure 7:51** Two forms of dicyandiamide monomer.

Mixtures of dicyandiamide polymers and metal salts are highly effective in precipitating some synthetic dyes.

The pH sensitivity of cationic polymers

The positive charge on cationic polymers can result from four different types of amines (primary, secondary, tertiary and quaternary amines). Three of these lose their positive charge at high pH levels. However, quaternary amines are positively charged at all pH levels. The pH at which the other three amines lose their charge depends on the type of amine and on the chemical groups that are adjacent to the amine group. Non-quaternary amine groups often lose their positive charge somewhere in the pH range 6–11.

Of the previously mentioned polymers, polyethylene imines and some Mannich-modified polyacrylamides belong to the group of polymers that lose their positive charge at high pH levels.

With increasing pH most of the cationic groups of polyacrylamides available on the market tend to decompose in such a way that the cationic group is hydrolysed (split off). At pH levels above 9–10 the rate of this reaction is relatively fast. When cationic polyacrylamide is dissolved, the pH of the water should be below 6 to avoid hydrolysis of the cationic groups.

If a cationic polyacrylamide is exposed to high pH for just a short time – less than a few minutes – it can be used as a flocculant. There are also polyacrylamines with cationic groups on the market that withstand high pH levels. However, these polymers are considerably more expensive than the most commonly used cationic polyacrylamides.

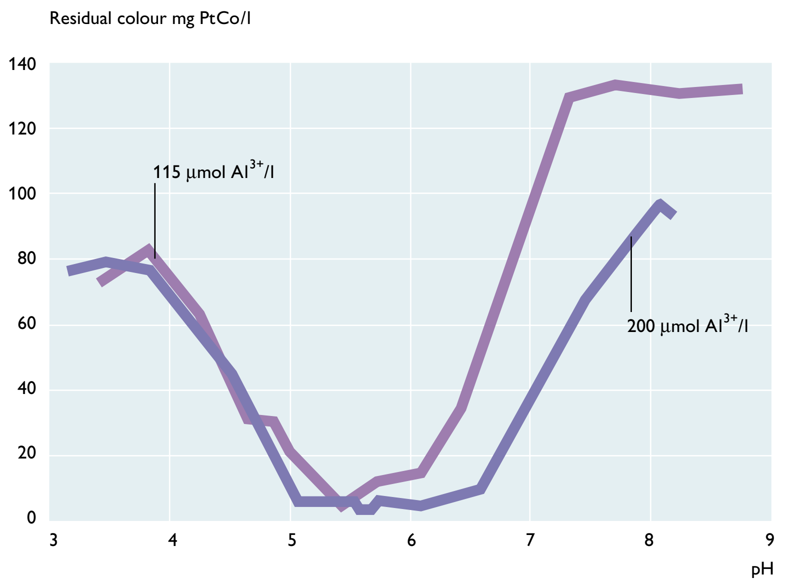
Floc strength and methods for obtaining a drier sludge

The strength of a floc produced without a flocculation aid (anionic polymer) depends on:

- **a) The amount of coagulant used**
- **b) The basicity of the metal salt**
- **c) The type of negative ion of the metal salt**
- **d) The size of the floc**

The lower the dose of coagulant that is used, the stronger the floc will be. However, if water is treated with a low dose of coagulant the flocculation pH must be kept under careful control, as can be seen in the diagram below.

Figure 7:37 illustrates the influence of pH on residual colour when coloured surface water is treated with two doses of aluminium sulphate.



➤ **Figure 7:37** Influence of pH on residual colour when coloured surface water is treated with two doses of aluminium sulphate.

Floc strength has not been studied for all types of polyaluminium salts. Some studies conducted on polyaluminium silicate chlorides indicate that silicate increases the floc strength.

The larger the flocs, the more fragile they are.

As previously mentioned, sludge that is produced with sulphate salts has a lower water content than that produced with the corresponding amount of metal in the form of a chloride salt. This is because sulphate ions screen the positive charges on the flocs more effectively than chloride ions. This effect allows the flocs to get closer to each other, which means there is less water between the hydroxides, so the sludge is drier.

It is possible to strengthen a sludge by using a flocculation aid, which also reduces the water content of the sludge.

Another advantage of using flocculation aids is that they substantially decrease the time needed for flocculation, and also increase the sedimentation rate of the flocs.

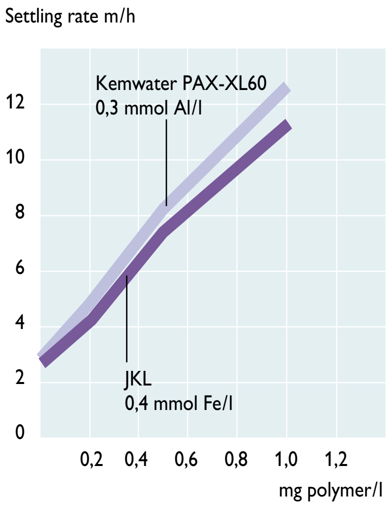
All flocculation aids are negatively charged. High molecular weight anionic polyacrylamides are often used as a flocculation aid, but activated water glass is also used, especially where the water is cold.

Before adding a flocculation aid the contaminants must be given time to react with the metal salt, and the metal hydroxide flocs must be allowed to grow. The flocculation aid is then added. The flocculation aid cross-links the flocs, which are positively charged. This condenses the flocs. Water is squeezed out and the flocs become stronger.

When a flocculation aid is used in combination with a metal salt the total time required for coagulation and flocculation is reduced to around 1/2–1/4 of the time that would be required without a flocculation aid.

The sedimentation rate of flocs formed using a flocculation aid may be considerably higher than that of flocs formed without a flocculation aid. This effect is illustrated in figure 7:52.

If flocculation is carried out in an intelligent way, the flocs may be obtained in the form of a compact aggregate or pellets that have both a low water content and sink very rapidly. (Research in this area is currently being carried out in Japan.)



➤ **Figure 7:52** The influence of the dose of anionic polymer on the settling rate of the flocs when wastewater is treated with two metal salts.

(Reference: Ødegaard, H., Grutle, S. and Ratnaweera, H. An Analysis of Floc Separation Characteristics in Chemical Wastewater Treatment, In: Chemical Water and Wastewater Treatment II, Klute R. and Hahn H.H. (Eds), Springer-Verlag, Berlin, Heidelberg, 1992, pp. 97–114, ISBN 3-540-55982-5.)